

**Changes in Iron and Phosphorus Sedimentation  
in Vadnais Lake 1985-1998**

**Final Report to**

**Board of Water Commissioners  
St. Paul, Minnesota**

**By**

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## INTRODUCTION

The St. Paul Water Utility has used iron additions to help control nuisance algal blooms in the Vadnais Lake chain for about a decade. Iron (as  $\text{FeCl}_3$ ) has been injected in-lake through hypolimnetic aerators (in operation since 1997) and added to inlet streams (principally Lambert Creek) in an effort to lower phosphorus concentrations by enhancing P sedimentation and burial. The addition of iron-containing compounds to control phosphorus levels has come under increasing scrutiny by the Minnesota Department of Natural Resources, which has concerns about both the effectiveness and potential impacts of this type of lake treatment. Most of the iron entering lakes (both natural and from treatments) ends up on the bottom, so quantifying the changes in Fe sedimentation caused by management practices should be a first step in evaluating potential impacts of iron treatment. The effectiveness of iron treatments on phosphorus control can also be evaluated by quantifying changes in phosphorus sedimentation that accompany iron additions. This long-term study quantifies the changes in iron and phosphorus budgets of Vadnais Lake by comparing iron and phosphorus sedimentation before and after iron treatment commenced. The project compares present-day P and Fe sedimentation rates to those measured in 1985 (prior to Fe treatments) and 1990 and uses a similar sampling and analytical strategy throughout the course of the study. It also employs data from long-term hydrological and chemical monitoring of the Vadnais Lake chain to constrain iron and phosphorus mass-balances under both past and present-day management practices.

### Objectives

- (1) Quantify changes in whole-lake Fe sedimentation cause by Fe additions/aeration from surface sediment samples collected from the profundal region of Vadnais Lake. The sites sampled in 1985 and 1990 were re-collected and analyzed in 1998 using the same methods employed in the earlier visits. Sediment accumulation rates are determined by  $^{210}\text{Pb}$  dating methods.
- (2) Assess the efficacy of Fe addition/aeration on in-lake P retention by quantifying whole-lake phosphorus sedimentation from the suite of surface samples collected for Fe analysis. Phosphorus accumulation rates (both total-P and P-fractions) for 1985, 1990, and 1998 are combined with input/output monitoring data to construct chemical mass-balances for each of the three time periods.
- (3) Estimate water-column P concentrations for Vadnais Lake in the distant past (prior to European settlement) to provide a base-line reference for management efforts to reduce phosphorus inputs and in-lake P levels. Historical phosphorus concentrations are quantitatively reconstructed from diatom assemblages preserved in a 1-m long sediment core collected (and dated by  $^{210}\text{Pb}$  methods) in 1990.
- (4) Determine whether Fe dosing of Lambert Creek has increased Fe concentrations of littoral sediments in the regions where the Creek enters Vadnais Lake. Iron concentrations are compared among surface sediment samples collected near the outfalls of Lambert Creek and Vadnais Creek (control site).

## Study Site

The St. Paul Water Utility (SPWU) receives source water from a chain of lakes and impoundments supplied by diversions from the Mississippi River and Rice Creek, as well as runoff from local watersheds. The system consists of three primary reservoirs that flow downstream from Pleasant Lake through Sucker Lake and finally to Vadnais Lake, from which the water is pumped to the SPWU filtration plant. The quality of the water delivered to the SPWU has been impaired historically by inputs of excess nutrients, particularly phosphorus, from changes in land-use in the contributing watersheds. As the terminal reservoir in the chain, Vadnais Lake exerts considerable influence on nutrient

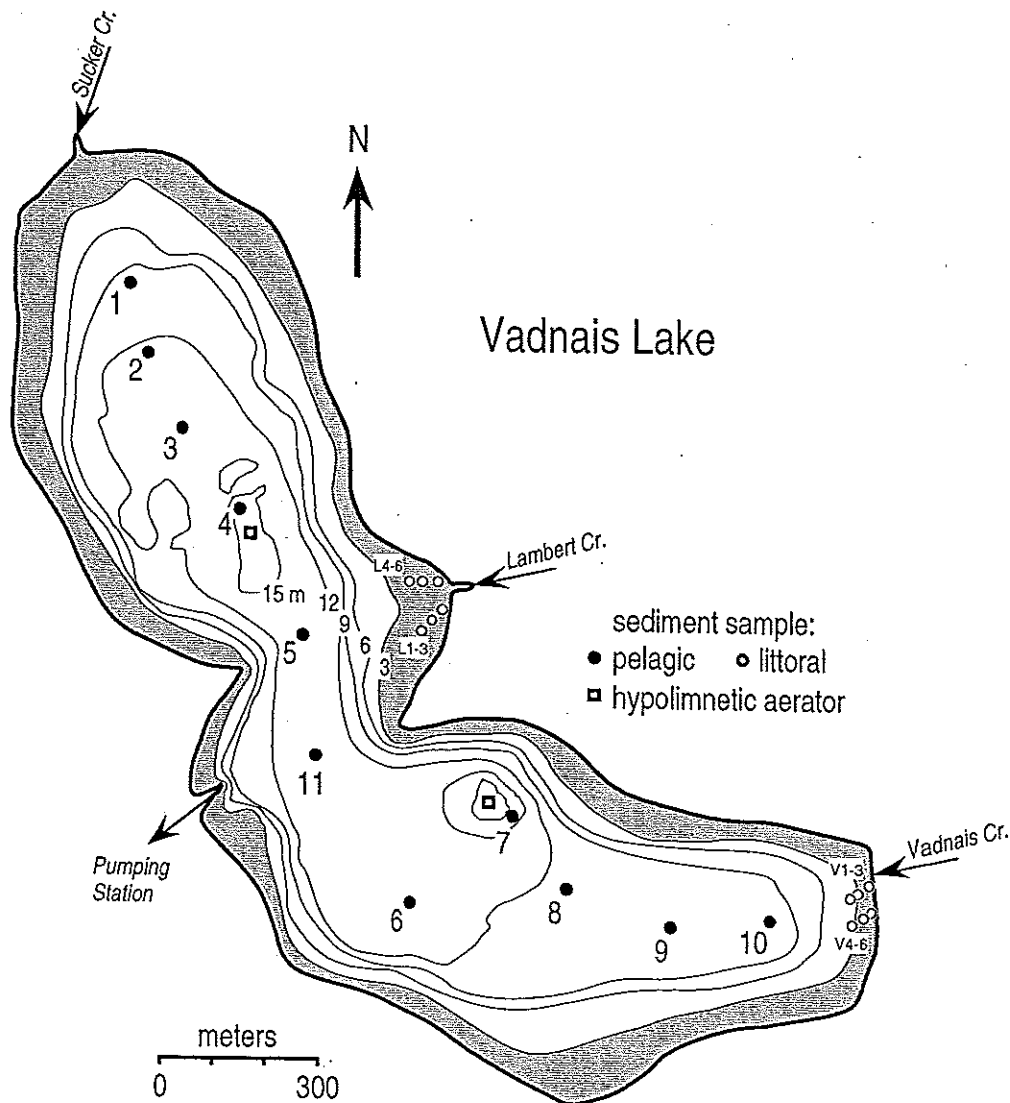


Figure 1. Locations of sample sites and hypolimnetic aerators in Vadnais Lake.

dynamics, algal productivity, and ultimately the presence of taste and odor problems that have plagued St. Paul water supplies in recent decades. Vadnais Lake is a moderately deep (mean depth = 8 m), 159 ha natural reservoir with an average residence time of 0.24 yr. Water enters the lake primarily through Sucker and Lambert Creeks and outflows almost entirely through the SPWU pumping station (Fig. 1). The basin itself is steep sided with only a modest littoral area and a relatively large flat profundal region; roughly 50% of the lake bottom is between 9 and 12 meter deep. Fine-grained organic-rich sediments accumulate throughout the deeper parts of the lake (> 3 meters), while coarse sandy materials and rocky substrates dominate the littoral fringe.

In 1984 the SPWU began a comprehensive monitoring and engineering program aimed at understanding and improving water quality in the Vadnais chain of lakes (Schuler, 1996). A system of 22 stream-flow and reservoir sampling stations was established to gain understanding of the supply system dynamics and to provide a mass-balance quantification of nutrient loading sources. In 1987 a ferric chloride feed system was

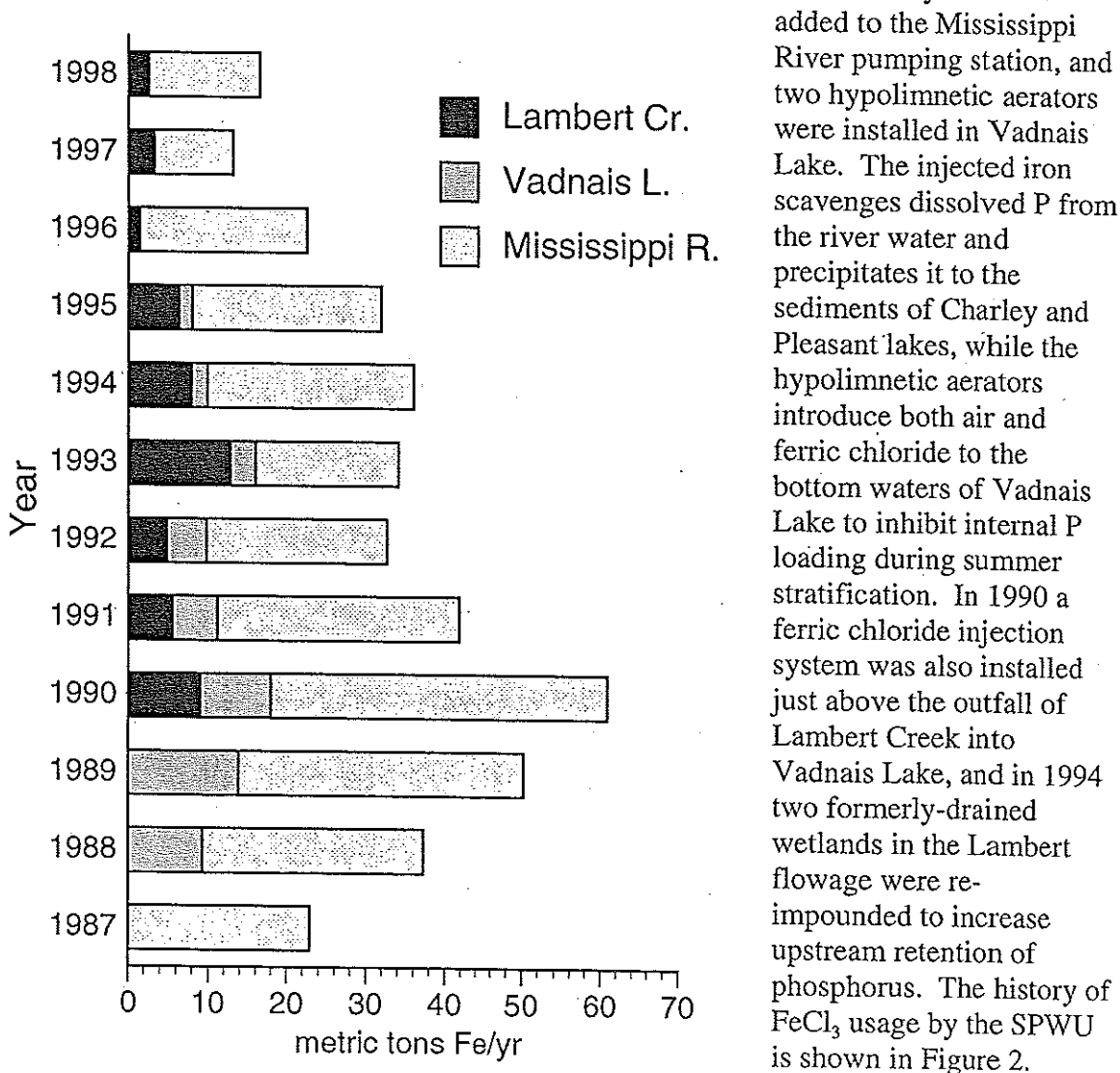


Figure 2. Ferric chloride usage by the St. Paul Water Utility, 1987-1998.

## METHODS

**Sediment Sampling** The surface sediments of Vadnais Lake were sampled from a set of fixed stations (Fig. 1) in October-1985, May -1990, and October-1998 by means of a gravity corer operated by line from the lake surface. The sampler was fitted with a 4-cm diameter polycarbonate core barrel and typically collected the upper 10-20 cm of soft sediment. The sediments were extruded from the top of the core tube and the uppermost 3 cm of material were retained for analysis. In 1985 and 1990 the extruded core lengths were not measured precisely, but were calculated later from sediment wet density and the cross-sectional area of the core barrel. In 1998 a calibrated extrusion device was used, and core lengths were measured directly. Sample stations were located by visual approximation to shoreline features and confirmed by measured lake depth (Fig. 3).

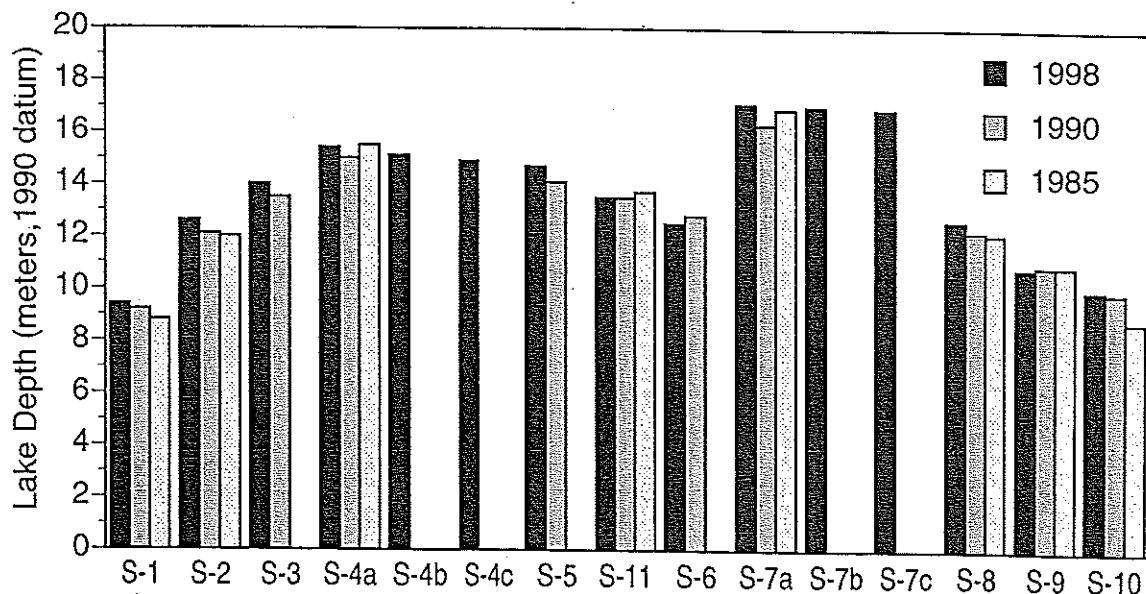


Figure 3. Measured lake depth at sampling stations in three collection years; lake elevations corrected to May-1990 datum.

The number of sample stations was increased incrementally on each subsequent visit, so that some stations are not represented by the earlier dates. In 1990 two new sample sites (S-4 and S-7) were located 10-15 meters from the recently installed hypolimnetic aerators, and in 1998 a transect of three cores was collected at approximately 15, 30, and 45 meters from the aerators in the vicinity of S-4 (S-4a, 4b and 4c) and S-7 (S-7a, 7b and 7c). Littoral sediments were also sampled for the first time in 1998 near the outfalls of Lambert and Vadnais creeks (Fig. 1). In each of these two areas, three short cores (2-cm in length) were collected along each of two transects at locations approximately 10, 20, and 30 meters from the shore in water depths ranging from 0.50 to 1.85 m.

In 1990 a 1-m long core was collected from site S-11 using a piston corer operated from the lake surface by light-weight magnesium drill rods. The core was maintained in



vertical position and extruded in the field at fixed increments of 1-5 cm in length. In 1998 the upper 15 cm of three surface cores (S-2, S-7b, and S-11) were sectioned into five contiguous depth increments, each section 3-cm in length. Based on  $^{210}\text{Pb}$  sedimentation rates (see below), these short cores encompass sediment intervals that had been at the surface at the time the sites were sampled in 1985 and 1990. All core samples were initially stored in polypropylene jars under refrigeration (4° C), but were subsequently dried for chemical analysis; 1985 and 1990 samples were oven dried at 90° C while 1998 sediments were freeze dried.

**Loss-on-Ignition** Dry-density (dry mass per volume of fresh sediment), water content, organic content, and carbonate content of Vadnais sediments were determined by standard loss-on-ignition techniques (Dean, 1974). Sediment samples of 1-2 g were dried overnight at 100° C and ignited at 550° and 1000° C for 1 hr each. Mass measurements were made of the wet samples and after each heating on an electronic analytical balance. Dry density was calculated from water content and fixed densities for organic, carbonate, and inorganic fractions.

**Lead-210 Dating** Surface sediments and core samples from all three collection years were analyzed for  $^{210}\text{Pb}$  activity to determine sediment ages and accumulation rates. Lead-210 was measured through its grand-daughter product  $^{210}\text{Po}$ , with either  $^{208}\text{Po}$  (1985 and 1990 samples) or  $^{209}\text{Po}$  (1998 samples) added as an internal yield tracer. The polonium isotopes were distilled from 0.5 - 4.0 g dry sediment at 550° C following pretreatment with concentrated HCl and plated directly onto silver planchets from a 0.5 N HCl solution (Eakins & Morrison, 1978). Activity was measured for 1-3 x 10<sup>6</sup> s with ion-implanted or Si-depleted surface barrier detectors and an Ortec alpha spectroscopy system. Unsupported  $^{210}\text{Pb}$  was calculated by subtracting supported activity from the total activity measured at each level; supported  $^{210}\text{Pb}$  was estimated from the asymptotic activity at depth in the 1990 core from S-11. Dates and sedimentation rates for the S-11 long core were determined according to the c.r.s. (constant rate of supply) model (Appleby & Oldfield, 1978) with confidence intervals calculated by first-order error analysis of counting uncertainty (Binford, 1990).

A  $^{210}\text{Pb}$  dilution model that assumes a constant flux of  $^{210}\text{Pb}$  to the profundal region of the lake (Binford & Brenner, 1986) was used to calculate sedimentation rates for the surface samples and ages for the deeper strata in each of the three short cores, S-2, S-7b, and S-11 (1998). According to this derivative of the c.r.s model, the sediment accumulation rate (r) for any surface sample can be estimated by:

$$r = \lambda \cdot D / \ln \left( \frac{P}{P - \lambda \cdot A} \right)$$

where:  $\lambda$  = the decay constant for  $^{210}\text{Pb}$  (0.03114 yr<sup>-1</sup>)

$D$  = the cumulative dry mass in the core interval (g cm<sup>-2</sup>)

$P$  = the flux of unsupported  $^{210}\text{Pb}$  to the core site (pCi cm<sup>-2</sup> yr<sup>-1</sup>)

$A$  = the inventory of unsupported  $^{210}\text{Pb}$  in the core interval (pCi cm<sup>-2</sup>).

The values for  $D$  and  $A$  are measured directly for each surface sample, while  $P$  is estimated from the rate of atmospheric  $^{210}\text{Pb}$  deposition with correction for sediment focusing. Because fine-grained sediments (with which  $^{210}\text{Pb}$  is associated) are eroded (focused) by wave action into deeper parts of the basin, the  $^{210}\text{Pb}$  flux to most sample sites should exceed the atmospheric rate. A  $^{210}\text{Pb}$  flux of  $0.9 \text{ pCi cm}^{-2} \text{ yr}^{-1}$  is assumed for all sites located below the 12-m depth contour, while a rate of  $0.6 \text{ pCi cm}^{-2} \text{ yr}^{-1}$  is applied to the three sites located above 12 m (S-1, S-9, and S-10). These fluxes (weighted by their respective depth contours) are equivalent to an average lake-wide  $^{210}\text{Pb}$  flux of  $0.5 \text{ pCi cm}^{-2} \text{ yr}^{-1}$  (the atmospheric flux for this region) and a focusing factor of about 2 for sites below the 12-m contour – a value consistent with the inventory of unsupported  $^{210}\text{Pb}$  in the 1990 long core from site S-11 ( $37 \text{ pCi cm}^{-2}$ ). The assumption of uniform rates of  $^{210}\text{Pb}$  deposition to the profundal region of the lake is reasonable in light of the lake's simple morphometry.

Whole-basin sediment accumulation rates were estimated by weighting the sediment flux at each sample site by bathymetric depth contour and summing the values lakewide. Thus the average sedimentation rates for sites S-1, S-9, and S-10 were multiplied by the area of the lake bottom lying between the 3-m and 12-m depth contours (40 ha), sites S-2, S-3, S-5, S-6, S-8, and S-11 were weighted by the lake area between 12 and 15 m (75 ha), and the deepest sites, S-4 and S-7 were applied to depths below 15 m (4 ha). Lake depths above 3-m were considered to be non-depositional for fine-grained sediments, as only sand and coarser material were found in these shallow regions.

*Phosphorus and Iron Analysis*      Sediments were extracted for phosphorus and metal determinations according to fractionation procedures adapted from Williams *et al.* (1971; 1976) and Engstrom and Wright (Engstrom & Wright, 1984) (Fig. 4). The extraction procedure permits the estimation of three forms of sediment phosphorus:

*NAI-P* (Non-Apatite Inorganic Phosphorus) represents the inorganic phosphorus associated with iron/aluminum oxyhydroxides and that dissolved in sediment pore-fluids.

*Organic-P* is phosphorus bound to particulate organic matter. Microbial decay may convert some organic phosphorus into inorganic forms (NAI-P), which are subsequently bound to sediments or released into the water column.

*Apatite-P* represent phosphorus bound to mineral particles, especially calcium-carbonates. This form is relatively stable and is not readily recycled into the water column.

Total phosphorus was measured as the ortho-P extracted by sequential digestion with 30% hydrogen peroxide (1 hr at  $85^{\circ}\text{C}$ ) followed by  $0.5 \text{ M HCl}$  (0.5 hr at  $85^{\circ}\text{C}$ ). Non-apatite inorganic phosphorus (NAI-P) was measured by extracting a second subsample in  $0.22 \text{ M}$  sodium citrate/ $0.11 \text{ M}$  sodium dithionite/ $0.11 \text{ M}$  sodium bicarbonate (CDB) for 15 min. at  $85^{\circ}\text{C}$ ; The sediment residue from the CDB extraction was further treated with  $0.5 \text{ M HCl}$  (16 hr at  $25^{\circ}\text{C}$ ) to determine apatite phosphorus. A third subsample was also treated with  $0.5 \text{ M HCl}$  (16 hr at  $25^{\circ}\text{C}$ ), but without the CDB step, to determine inorganic-P; Non-apatite inorganic P was estimated as the difference between the inorganic-P and apatite-P. Finally the residual (organically-bound) phosphorus was

estimated from the difference between the total-P and the inorganic-P. The average relative difference for replicated extractions of five deep-water samples was 2% for total-P, 4% for apatite-P, and 6% for inorganic-P. Extracts were analyzed colorimetrically by spectrophotometer (1985 and 1990 samples) and Lachat Autoanalyzer (1998 samples). Independent measurements of total-P by ICP-MS for 1998 samples were almost identical to colorimetric determinations with an average relative difference of 1.5%.

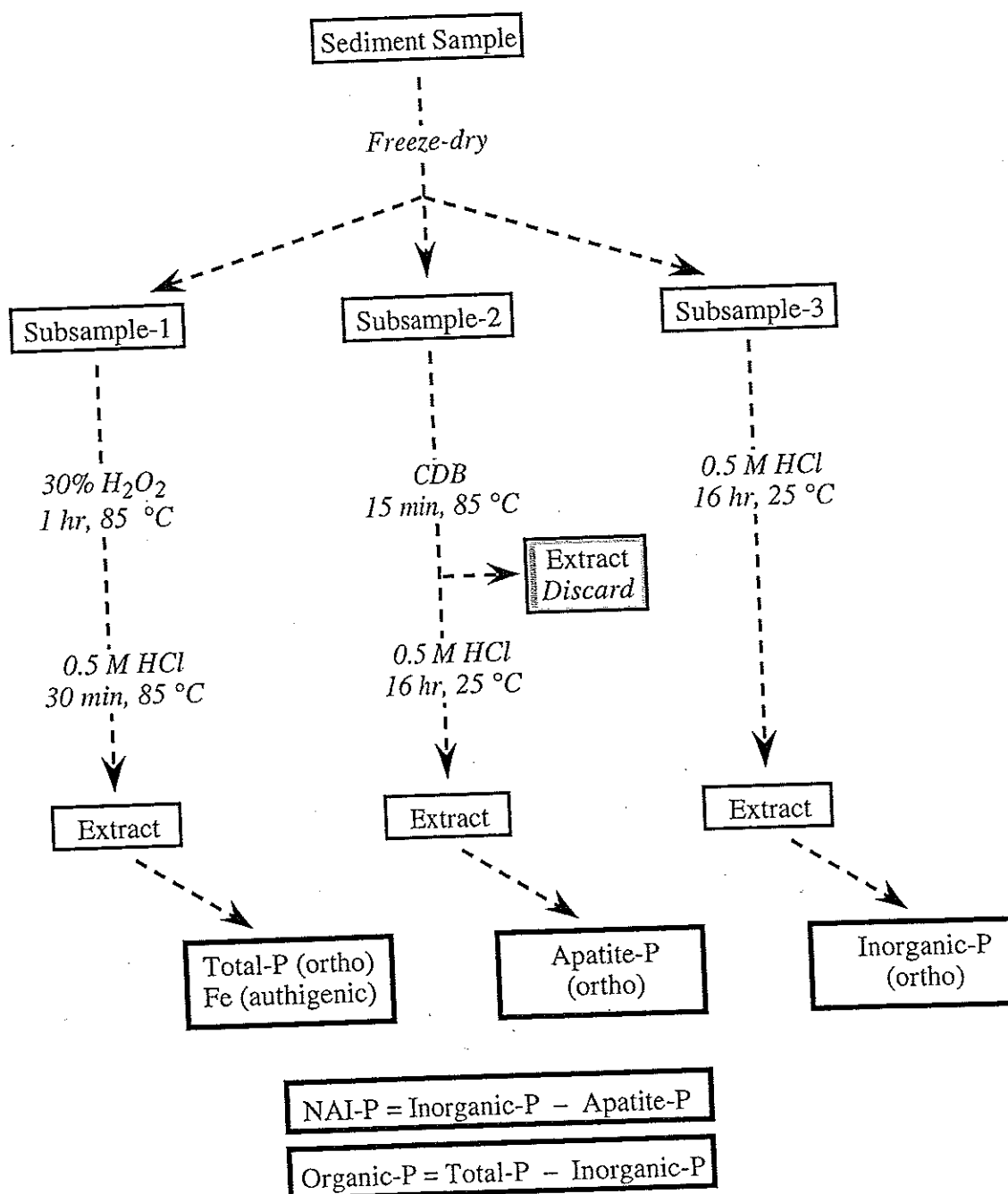


Figure 4. Flow diagram for sedimentary phosphorus extraction.

Acid-extractable Fe and Mn and a suite of six other major elements (Al, Si, P, Mg, Ca, K) were analyzed from the same H<sub>2</sub>O<sub>2</sub>/HCl extract as that used for Total-P determinations. Concentrations were measured on a Perkin-Elmer ELAN-5000 inductively coupled plasma mass spectrometer (ICP-MS); all samples were measured at least five times; samples and standards were spiked with Rh and Sc to correct for instrument drift. Replicated extractions of four samples had an average relative difference of 5% for Fe and 8% for Mn.

*Diatom Analysis* Three wet subsamples (0-1 cm, 6-8 cm, 85-90 cm) from the 1990 S-11 core and a single freeze-dried subsample (0-3 cm) from the 1998 S-11 core were used for microfossil analysis. Subsamples were heated at 150° C in 20 ml 30% H<sub>2</sub>O<sub>2</sub> for 30 min followed by addition of 25 ml concentrated HNO<sub>3</sub>. The solution was then heated for another hour at 175° C. Material was cooled and rinsed with distilled water six times with six hours of settling between rinses. Lastly, cleaned material was dried onto coverslips using settling chambers (Battarbee, 1973) to create a random distribution of siliceous microfossils and the coverslips mounted on microslides with Naphrax.

Siliceous remains (diatom valves, chrysophyte cysts, and sponge spicules) along one or more microslide transects were counted and identified to the lowest possible taxonomic category on an Olympus BX50 microscope using full oil immersion optics capable of N.A. 1.32 and 1250X until a total of 500 diatom microfossils was tallied. Raw data counts were converted to percent abundance by diatom species relative to total diatom counts.

Weighted average calibration and reconstruction (Birks *et al.*, 1990) were used to infer historical water column total phosphorus (TP) in Vadnais Lake. A calibration model for total-P reconstruction was developed by Ramstack (1999) from surface-sediment diatom assemblages and environmental data from 55 Minnesota lakes. Ramstack (1999) used canonical correspondence analysis to identify the major environmental variables that significantly explained diatom species distribution; these variables included log total-P. Species and environmental data were subsequently analyzed using weighted average regression software (Juggins, 1998) with and without tolerance downweighting to calculate TP optima (from 9 to 105 µg total-P L<sup>-1</sup>) and tolerances for 108 diatom taxa in Ramstack's (1999) training set. Tolerance downweighting puts greater weight on taxa with narrower environmental tolerances.

Downcore data for Vadnais Lake core samples were subject to weighted average calibration with and without tolerance-downweighting to reconstruct historical water column TP (Birks *et al.* 1990). Downcore distribution of forty diatom taxa included in the Ramstack (1999) model were used; four taxa (*Fragilaria vaucheriae*, *Synedra rumpens*, *Synedra ulna*, and *Rhopalodia gibba*) were present at >1% abundance in one or more Lake Vadnais subsamples but were not included in the Ramstack (1999) data set.

## RESULTS AND DISCUSSION

### Surface-Sediment Composition

The surficial sediments from the deep-water regions of Vadnais Lake are of fairly uniform composition (Fig. 5). Organic content averages  $16.3 \pm 1.4\%$  (s.d.), carbonates are  $35.1 \pm 3.1\%$ , and inorganic materials make up the remaining  $48.6 \pm 3.3\%$ . There is no discernable pattern across the lake basin, and differences between 1985 and 1990 are

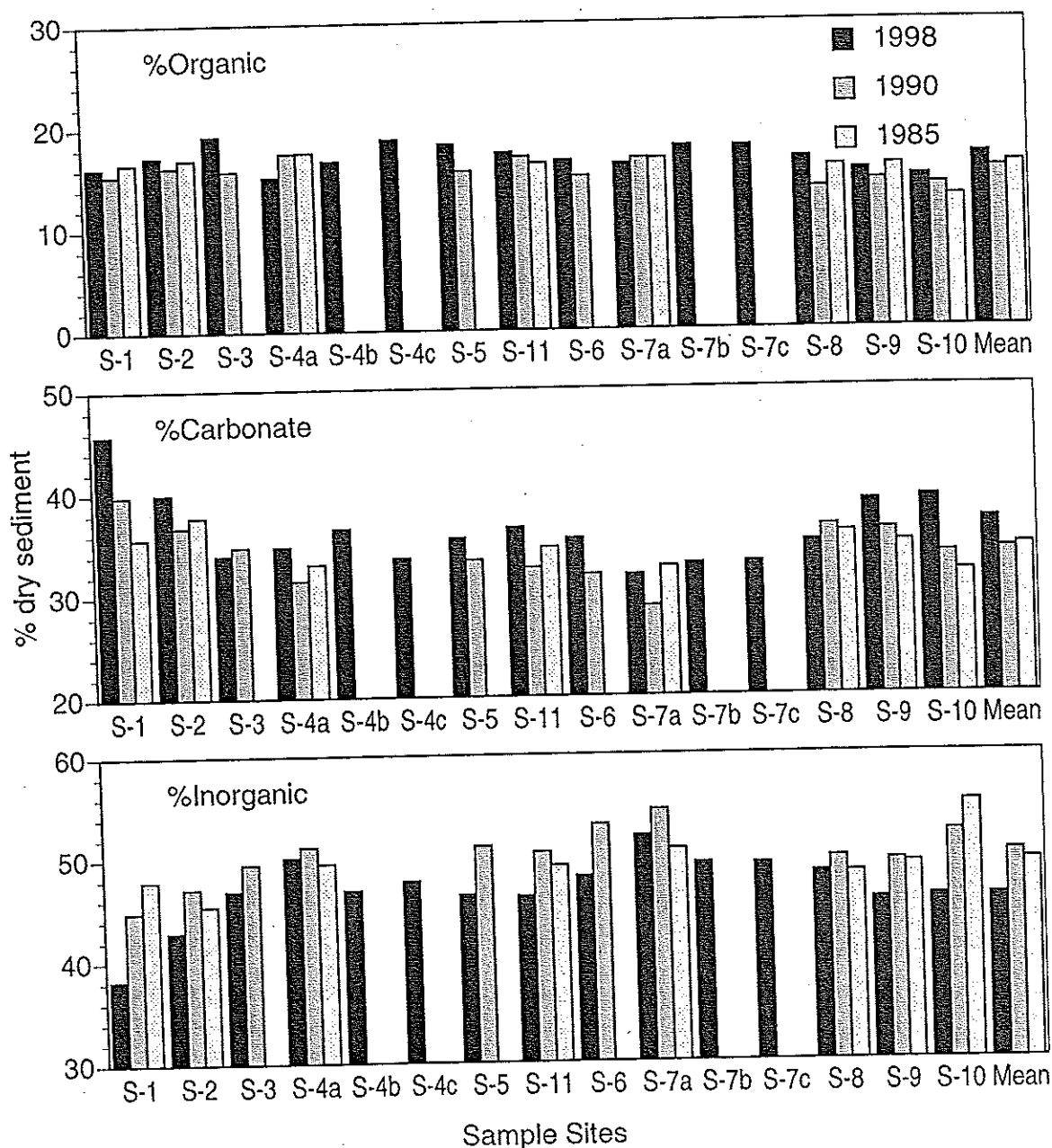


Figure 5. Composition of Vadnais Lake surface sediments from loss-on-ignition.

small and variable among sample sites. However, samples from 1998 are consistently higher in organic matter and carbonates and lower in inorganic content (about 4% on average) than the 1985 and 1990 collections. Sediment accumulation rates are likewise similar among sampling sites and from year to year, averaging  $1.2 \pm 0.3 \text{ kg m}^{-2} \text{ yr}^{-1}$  (Fig. 6). Only the two sites nearest the hypolimnetic aerators in 1998 (S-4a and S-7a) stand out with significantly elevated sediment fluxes (about twice the 1998 mean).

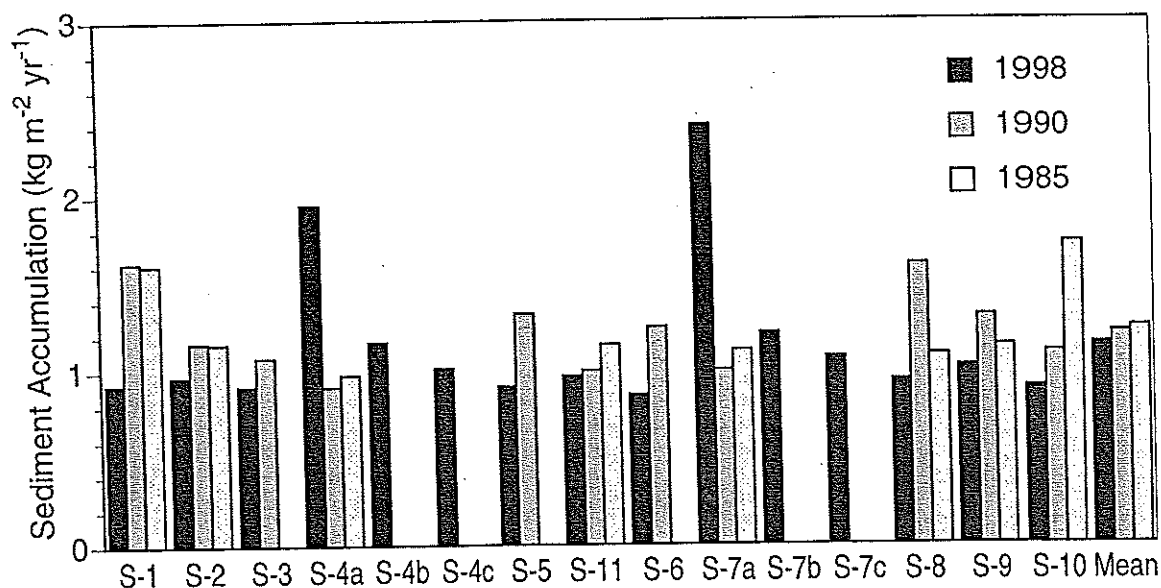


Figure 6. Sediment accumulation rates at sample sites estimated from  $^{210}\text{Pb}$  dating.

Phosphorus concentrations, on the other hand, show striking changes between collection years (Fig. 7). In 1985 deep-water sediments were spatially uniform in total-P ( $0.88 \pm 0.09 \text{ mg g}^{-1}$  dry mass) and similar in proportion of the three major fractions (38% NAI-P, 16% apatite-P, and 46% organic-P). In 1990 several sites, especially those near the aerators (S-4 and S-7), showed significant increases in total-P, so that the lake-wide mean rose to  $1.21 \pm 0.56 \text{ mg g}^{-1}$ . Virtually all of this increase was in the NAI-P fraction, as apatite-P and organic-P remained unchanged. By 1998 total-P concentrations had risen markedly at all sites below the 12-m depth contour (but less so at the shallower sites, S-1, S-9, and S-10), owing again to increased levels of NAI-P. P concentrations also increased with distance along the transect of sites near the two aerators, S-4 (a-c) and S-7 (a-c). In these most recent collections, total-P averaged  $2.35 \pm 0.92 \text{ mg g}^{-1}$  (3x 1985 values), and 71% was in the NAI-P fraction.

The changes in iron and manganese concentrations between collection years mirror those exhibited by total-P and NAI-P (Fig. 8). In 1985, Fe concentrations averaged  $12.5 \pm 2.4 \text{ mg g}^{-1}$ , by 1990 they had risen to  $16.3 \pm 3.7 \text{ mg g}^{-1}$ , and in 1998 they were at  $23.1 \pm 7.2 \text{ mg g}^{-1}$ . Mn concentrations averaged  $1.5 \pm 0.2 \text{ mg g}^{-1}$  in 1985,  $2.5 \pm 2.1 \text{ mg g}^{-1}$  in 1990, and  $4.6 \pm 3.3 \text{ mg g}^{-1}$  in 1998. Iron increases between 1985 and 1990 were fairly uniform among sample sites, whereas those for Mn were largely restricted to the aerator sites, S-4 and S-7. By 1998 Mn as well as Fe had increased markedly at all sites below the 12-m

depth contour, and like phosphorus, both elements showed higher concentrations along the transect of sites away from the two aerators. The Fe increases from 1990 to 1998 were smaller relative to those for P or Mn, so that Fe/P ratios decreased from a lakewide average of 14.3 in 1985 and 1990 to 10.4 in 1998; Fe/Mn ratios fell from an average of 8.6 to 6.4 during this same period.

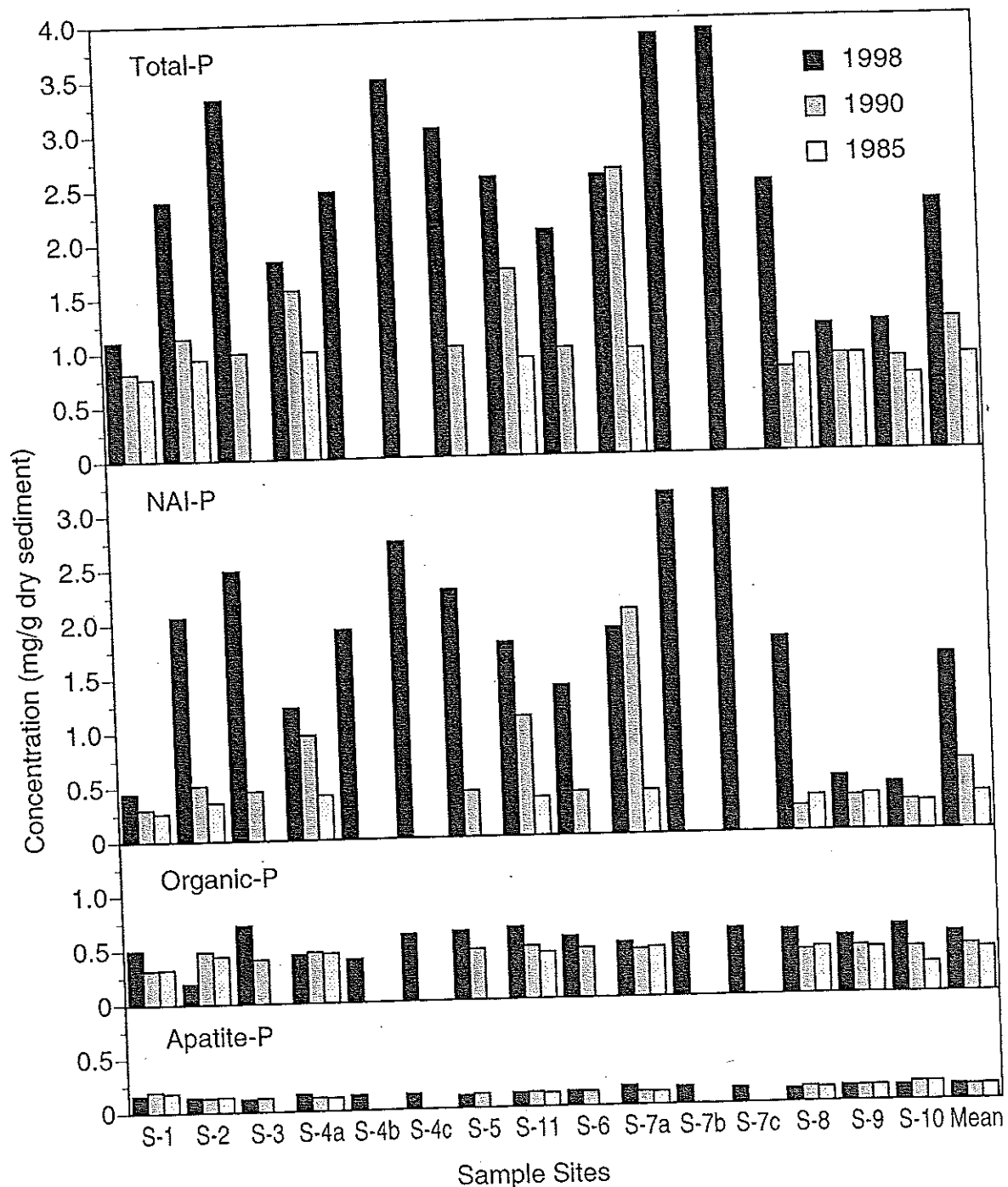


Figure 7. Concentrations of total-phosphorus and P-fractions in surface sediments from Vadnais Lake.

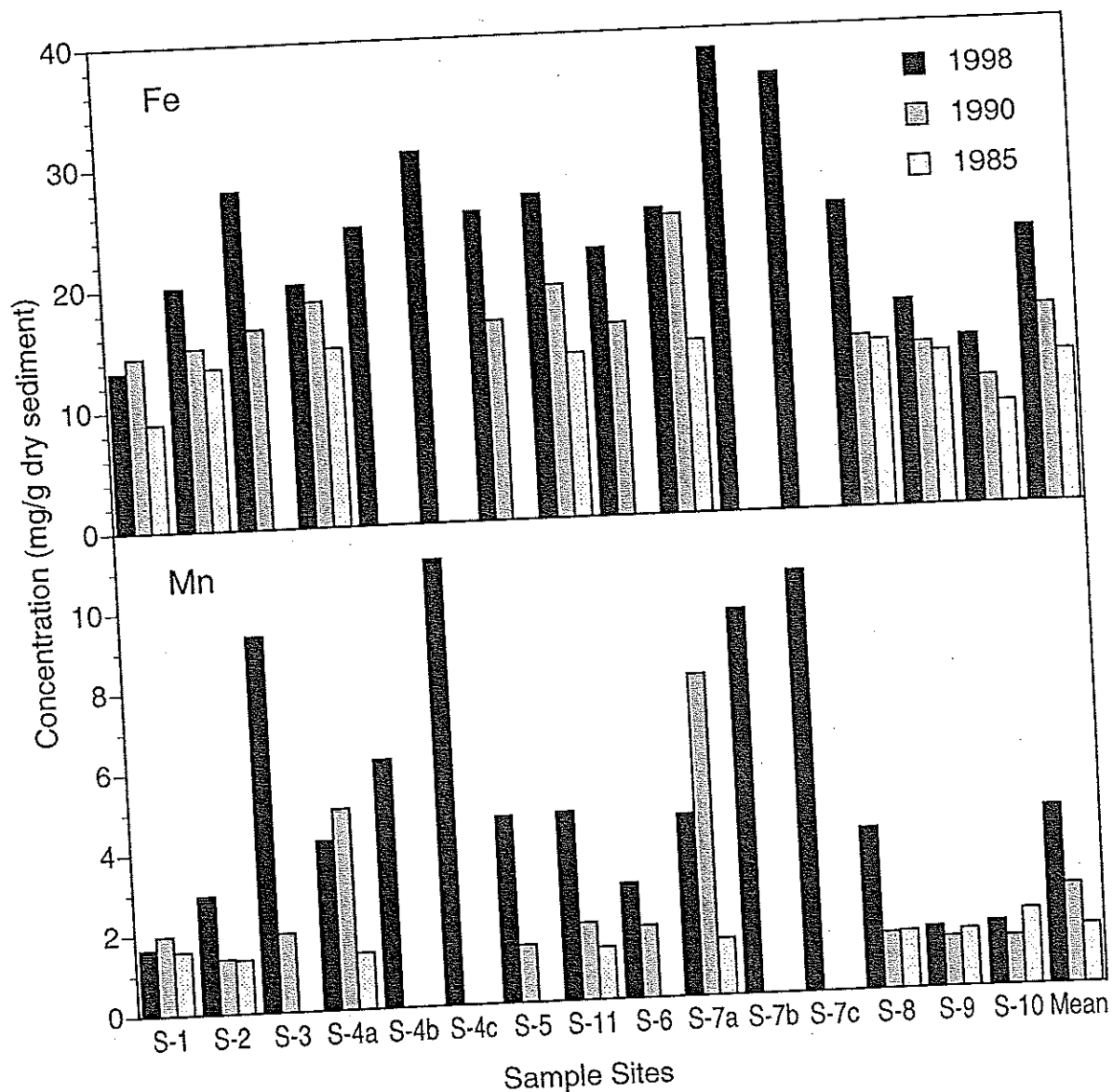


Figure 8. Iron and manganese concentrations in surface sediments from Vadnais Lake.

### Sediment Fluxes and Mass Balance

The rising sedimentary concentrations of P, Fe, and Mn between collection years coupled with steady lake-wide sedimentation rates has resulted in a marked increase in burial of these elements in the sediments of Vadnais Lake (Fig. 9). Lake-wide total-P fluxes – estimated by weighting the P flux at each sample site by the portion of the depositional basin it represents (see methods) – were 1.26 metric tons (t)  $\text{yr}^{-1}$  in 1985, 1.52 t  $\text{yr}^{-1}$  in 1990, and 2.43 t  $\text{yr}^{-1}$  in 1998. Virtually all of this increase was in the NAI-P fraction which increased by 40% between 1985 and 1990 and 150% from 1990 to 1998. Present-day (1998) Fe fluxes of 24.2 t  $\text{yr}^{-1}$  are 7% higher than they were in 1990 (22.6 t  $\text{yr}^{-1}$ ) and 36% above 1985 values (17.8 t  $\text{yr}^{-1}$ ). Over this same 13-year time period (but mostly after 1990) Mn sedimentation doubled from 2.18 to 4.27 t  $\text{yr}^{-1}$ .



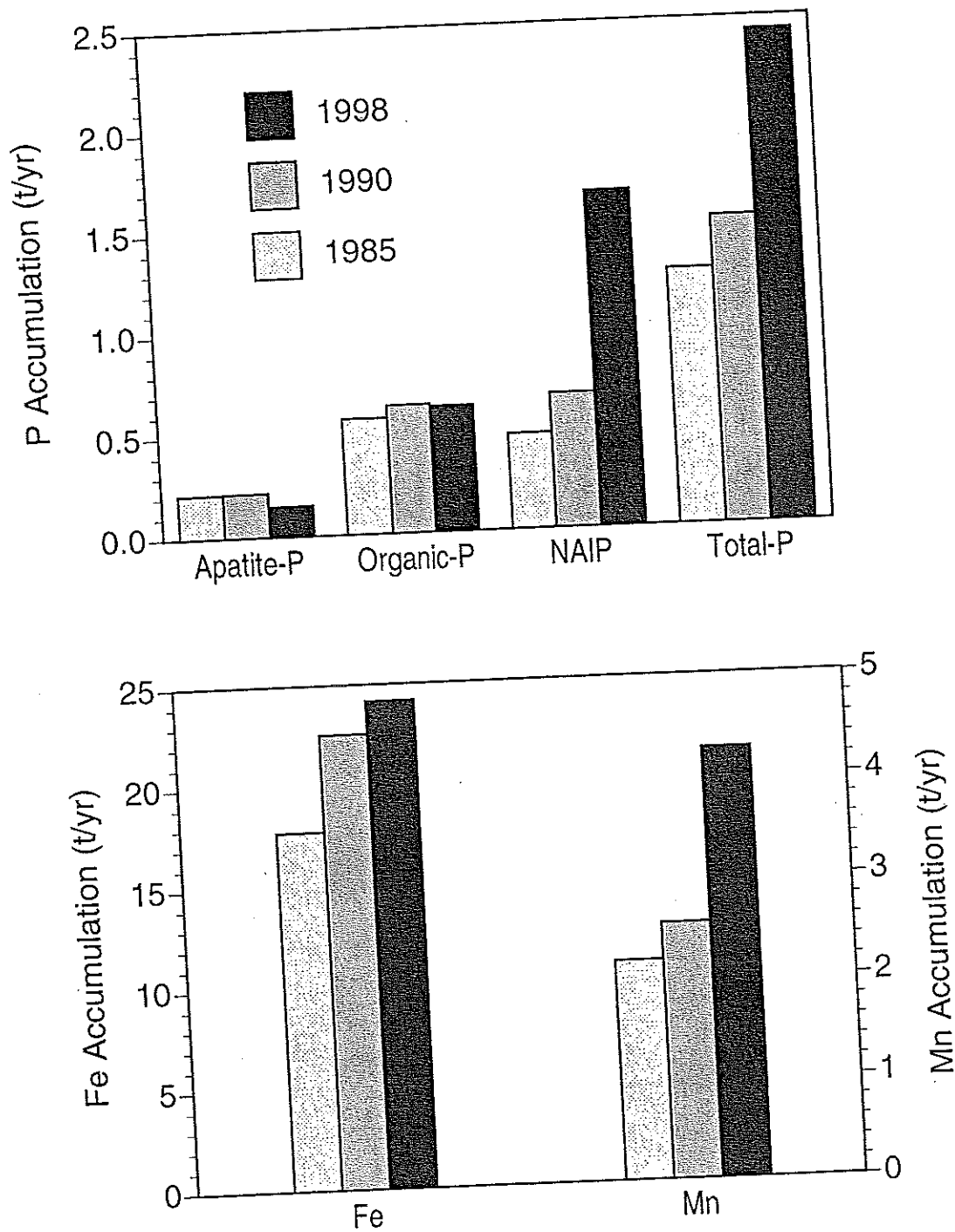


Figure 9. Whole-basin sedimentary fluxes of P, Fe, and Mn in Vadnais Lake.

These results provide strong evidence that engineering solutions (hypolimnetic aeration and iron injections) undertaken to increase phosphorus retention in Vadnais sediments have markedly altered the redox environment of the deeper parts of the basin, resulting in more effective burial of the P, Fe, and Mn loads entering the lake. Indeed previous analyses of the phosphorus mass-balance for Vadnais Lake (Walker, 1990) arrived at the

same conclusions based on direct hydrologic and water-quality monitoring (Fig. 10). Net phosphorus sedimentation, estimated by the difference between monthly inflows, outflows, and changes in water-column storage of total-P for 1984-85 ( $1.26 \text{ t yr}^{-1}$ ) and 1988-89 ( $1.45 \text{ t yr}^{-1}$ ) are almost identical to rates determined for these same intervals by direct analysis of the sediments (Fig. 11). Although the increase in P sedimentation between 1985 and 1990 was small, P inputs declined simultaneously, and in-lake P retention was much enhanced. Both approaches (mass-balance and sediment cores) confirm that in-lake retention (sediment burial) doubled from about 19% to 38% of influent total-P following the onset of hypolimnetic aeration and iron injection.

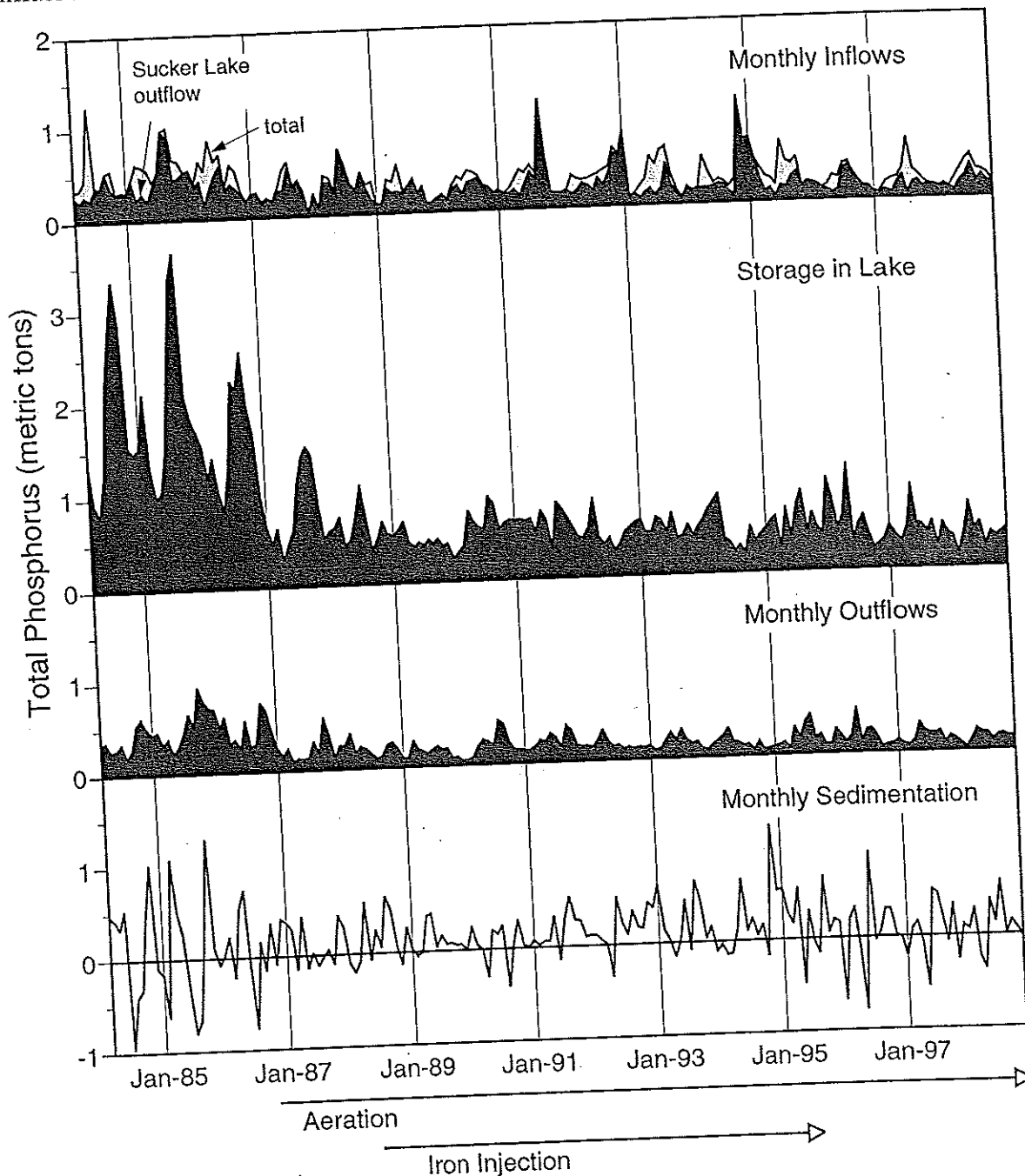


Figure 10. Monthly phosphorus budget for Vadnais Lake.

However, the coherence between sediment-core and mass-balance results does not hold for the 1998 sediment collections. Phosphorus sedimentation calculated by mass-balance for calendar years 1997-98 ( $8.83 \text{ t yr}^{-1}$ ) is about one-third the rate estimated from the sediment core data, and in-lake retention, according to the mass-balance, declined (from 1988-89 levels) to about 30% (Fig. 11). The sediment-core results imply a P retention rate in excess of 80%, a value that is difficult to reconcile with measured P inflows, lake-water P concentrations, and SPWU withdrawals (outflow). A difference of this magnitude is also difficult to explain by errors of estimation or measurement, especially as mass-balance and core data from the two earlier time periods match so well.

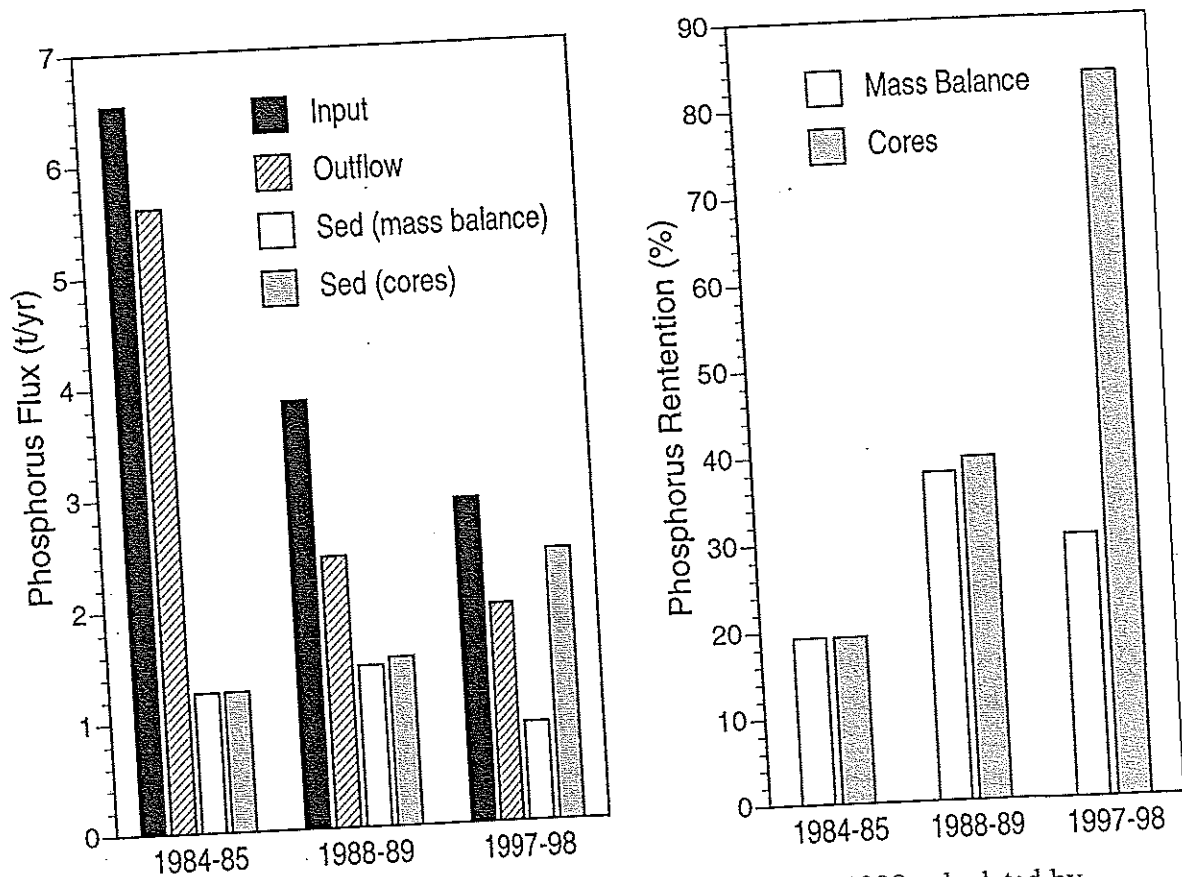


Figure 11. Annual phosphorus budget for Vadnais Lake 1984-1998 calculated by hydrologic mass-balance and from sediment-core data.

Because the increase in sedimentary P concentrations between 1990 and 1998 is so clear-cut, an additional P source (other than inflows) seems highly probable. That source is most likely redox dissolution of Fe-P complexes in sub-surface sediments and upward diffusion along a concentration gradient generated by precipitation at the oxidized surface (Carignan & Flett, 1981). In Vadnais Lake, such diagenetic enrichment was likely enhanced by hypolimnetic aeration and  $\text{FeCl}_3$  additions, which today inhibit diffusion of P across the sediment-water interface. It also appears that P enrichment has been building gradually since the onset of aeration, as it was not yet detectable in 1985 or 1990 sediment samples above that expected from external sources alone. Similar enrichment of

surface sediments has been reported from other lakes subject to long-term hypolimnetic aeration, but in these cases much of the P was not permanently buried, but seasonally released back to the water column (Gächter & Wehrli, 1998). Thus the recent build-up of high levels of labile P in Vadnais surface sediments (along with declining Fe/P ratios), imply that internal P-loading could become quite severe if aeration were ever interrupted.

Manganese, which shows an almost identical pattern of increase to that of total-P (Fig. 11), may also be diagenetically enriched. Although there are no mass-balance data for Mn from which to confirm this possibility, Mn is readily mobilized at low redox potentials and is commonly enriched in the surface sediments of lakes. Iron sedimentation, on the other hand, shows only a modest 7% increase ( $1.6 \text{ t yr}^{-1}$ ) between 1990 and 1998, and thus may more closely correspond to actual changes in external Fe loading to the lake. The total increase in Fe sedimentation between 1985 and 1998 ( $6.3 \text{ t yr}^{-1}$ ) is only slightly greater than the average rate of hypolimnetic Fe injection between 1988 and 1998 ( $4.9 \text{ t yr}^{-1}$ , Fig. 2), and if the Fe injections at the mouth of Lambert Creek are factored in, the intentional increase in external Fe loads is more than enough to account for the changes in Fe sedimentation in Vadnais Lake.

### Historical Trends from Cores

Three of the surface cores collected in 1998 were sectioned at 3-cm increments to a depth of 15 cm to obtain older sediments corresponding to the 1985 and 1990 surface samples. Results from these 15-cm short cores can be used to evaluate the extent to which upward diffusion may have altered P, Fe, and Mn concentrations in the surface sediments. Sediment ages in the core slices are extrapolated from  $^{210}\text{Pb}$  sedimentation rates in the 0-3 cm slice and plotted together with the 1985 and 1990 samples (Fig. 12). For cores S-2 and S-11, elemental concentrations in strata from 1985 and 1990 are generally similar to concentrations measured in the surface samples collected in those years. Such results imply that the core profiles have not been appreciably altered by diffusional processes. In contrast, core S-7b from near one of the two aerators shows P, Fe, and Mn concentrations at depth elevated well above that measured when those sediments were at the surface in 1985 and 1990. These data suggest that the entire 15-cm sediment column may have become diagenetically enriched by upward diffusion. The difference among these test cores is likely related to proximity to the aeration source which could drive oxygen deep into the sediments at S-7b but much less so at S-2 or S-11. Although somewhat contradictory, these results imply that if near-surface sediments (at sites more distant from the aerators than S-7b) are enriched by post-depositional diffusion, it was not yet evident in 1985 or 1990, at least at the coarse stratigraphic resolution at which these cores were sampled.

A single meter-long core was collected from site S-11 in 1990 to reconstruct conditions exiting in Vadnais Lake prior to hydrologic and land-use alterations in the watershed. Lead-210 dating results indicate that the core extends back to about 1860 and that sedimentation rates, though uncertain early on, have more than doubled since 1900 (Fig. 13). This increase in sediment flux corresponds to a 15-20% rise in inorganic content and likely represents increased erosion coupled with ditching of the Lambert Creek watershed in the early 1900s.

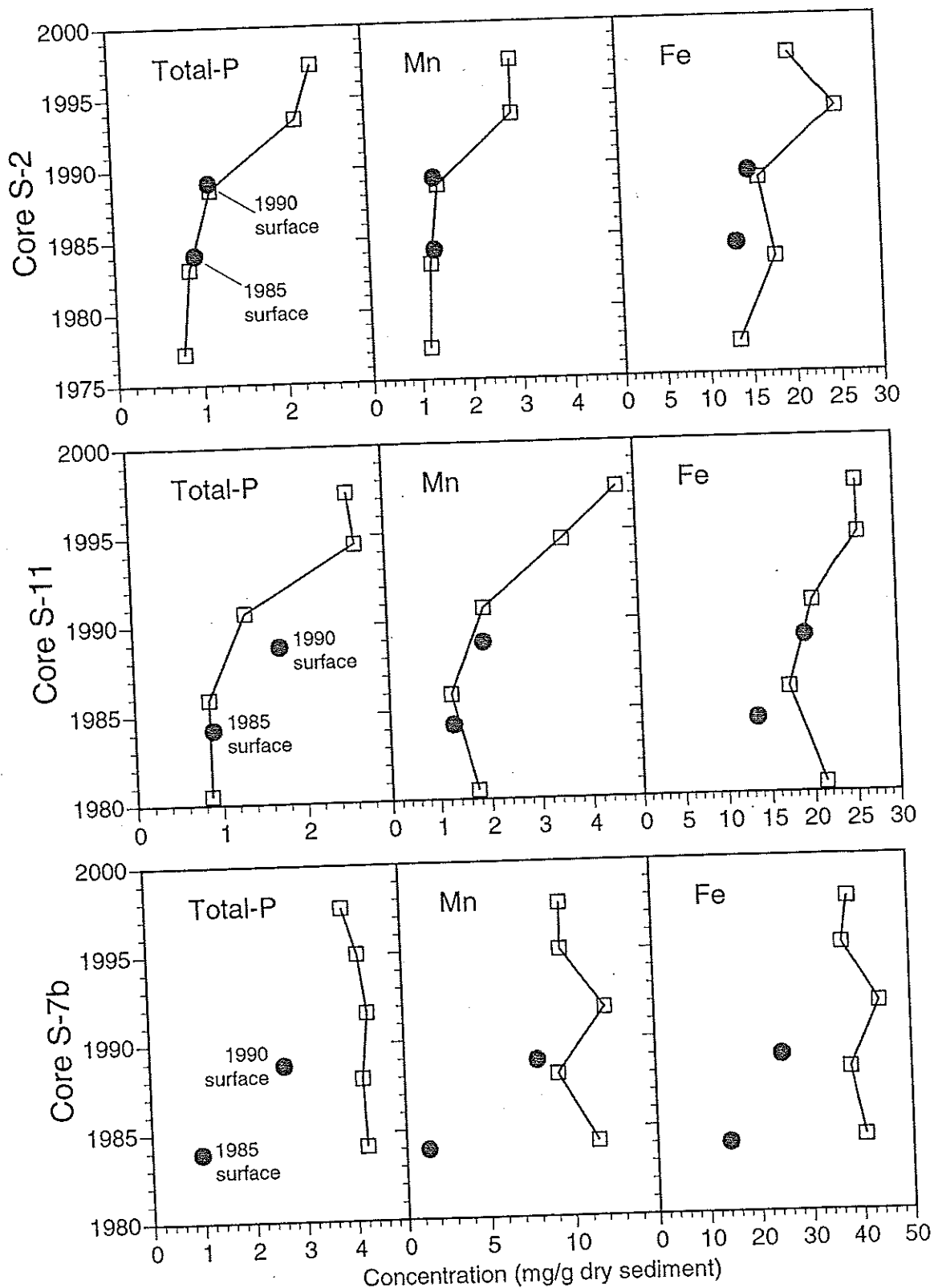


Figure 12. Comparison of P, Fe, and Mn concentrations in 1998 short cores with concentrations in surface samples collected from the same sites in 1985 and 1990.

Phosphorus and iron concentrations also decrease markedly up-core (until the mid-1900s), largely as the result of dilution from inputs of inorganic (clastic) materials and carbonates. Total-P concentrations decline from  $1.2 \text{ mg g}^{-1}$  in 1860 to  $0.7 \text{ mg g}^{-1}$  in 1940 while Fe content decreases from  $36$  to  $14 \text{ mg g}^{-1}$  over this same time period (Fig. 14). Accumulation rates (which correct for dilution) indicate that the flux of Fe and total-P have not changed systematically over time. Total-P accumulation rates average around  $1.1 \text{ g m}^{-2} \text{ yr}^{-1}$  and Fe about  $22 \text{ g m}^{-2} \text{ yr}^{-1}$  for the period of record. Only in the uppermost 2 cm of core do elemental concentrations and fluxes increase appreciably.

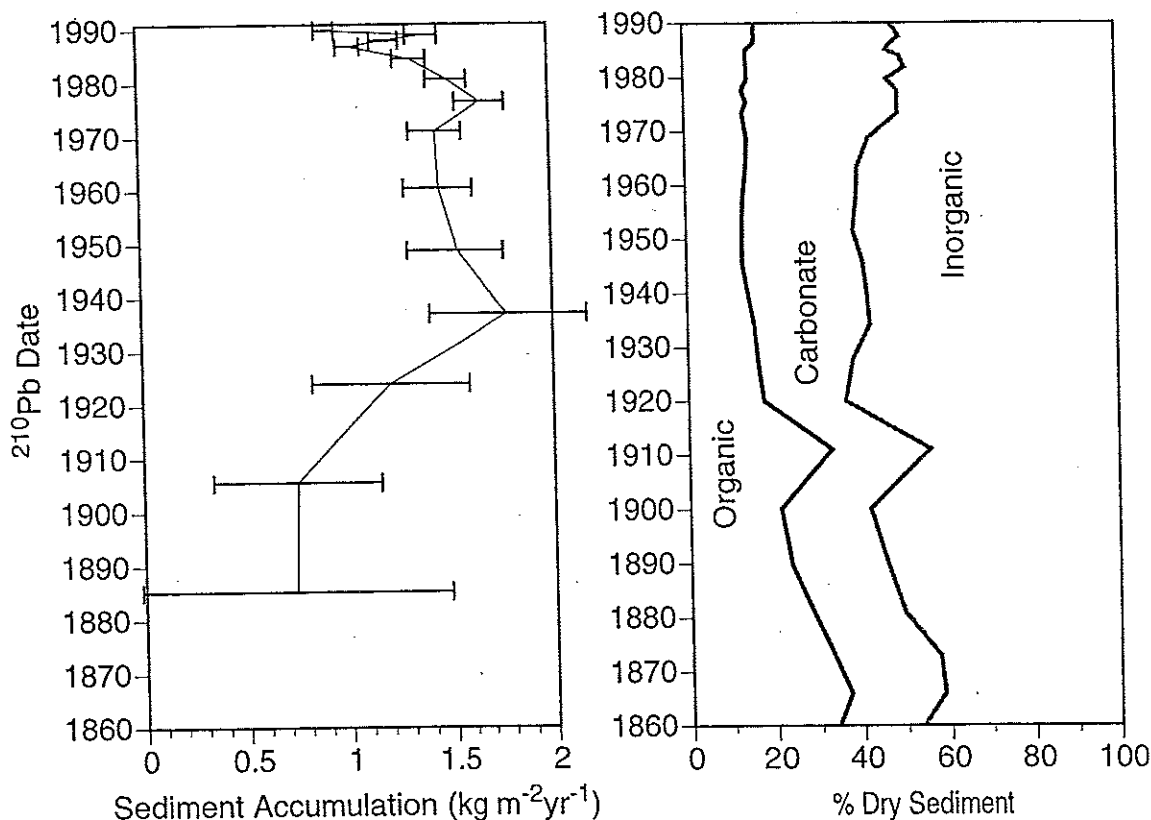


Figure 13. Lead-210 chronology and accumulation rates and loss-on-ignition of a meter-long sediment core collected from site S-11 in 1990.

Viewed in the context of these long-term data, the recent  $\text{FeCl}_3$  injections to Vadnais Lake and Lambert Creek have had measurable though modest effects on sedimentary P and Fe concentrations and fluxes. Mean lake-wide Fe concentrations in surface sediments ( $23 \text{ mg g}^{-1}$ ) are still well below historical baseline ( $36 \text{ mg g}^{-1}$ ), and only in the vicinity of the hypolimnetic aerators (S-4 and S-7) do present-day concentrations approach these 1860 values. Present-day Fe accumulation rates are about  $24 \text{ t yr}^{-1}$  as compared to a baseline (1860) flux of  $21 \text{ t yr}^{-1}$ , or an average  $18 \text{ t yr}^{-1}$  for the entire period of record. These historic whole-basin fluxes are obtained by scaling Fe accumulation rates at S-11 to the present-day lake-wide average. Thus the recent iron injections

represent at most 25% of the modern Fe flux to Vadnais Lake and as little as 14% of the pre-settlement Fe accumulation rate. Because hypolimnetic aeration may have increased Fe retention to something approaching pre-settlement conditions, 14% is probably a better estimate of actual changes in Fe loading brought about by  $\text{FeCl}_3$  additions.

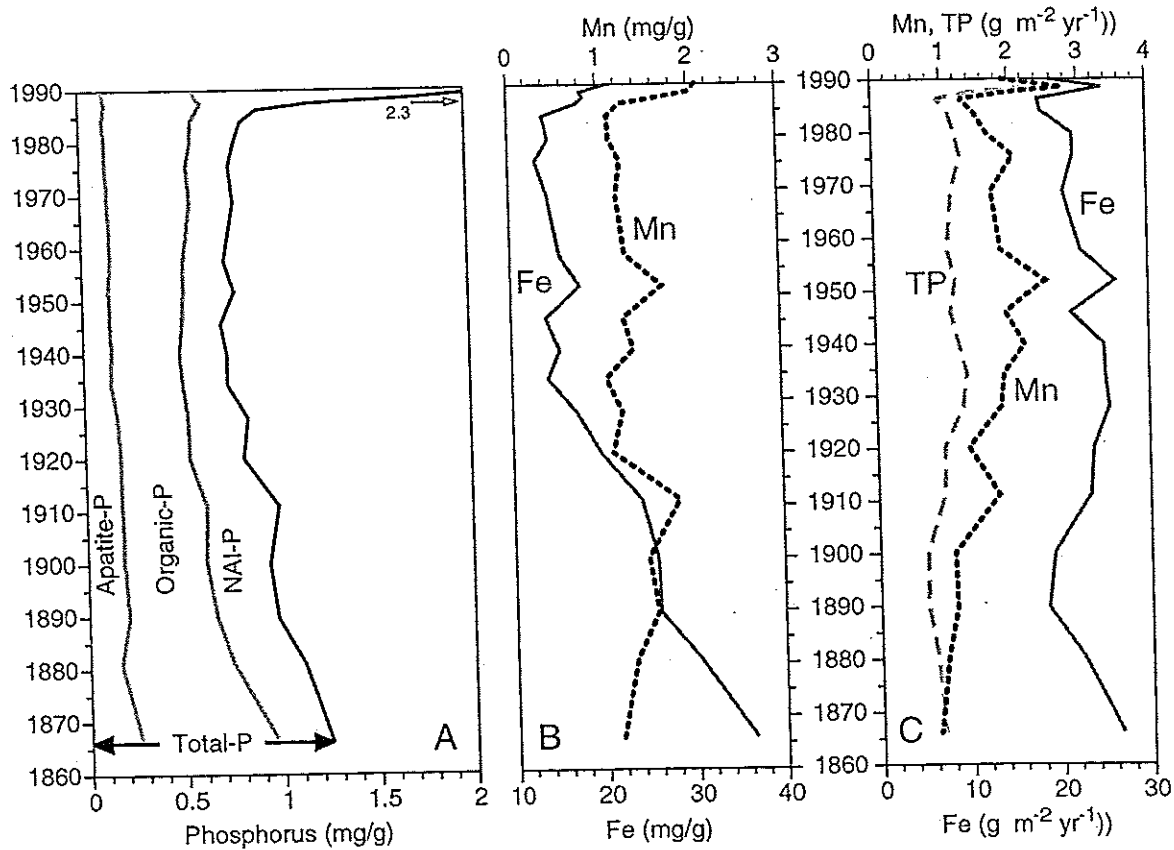


Figure 14. Chemical stratigraphy of a  $^{210}\text{Pb}$ -dated sediment core from site S-11; (A) Phosphorus concentrations (P-fractions are stacked to equal total-P), (B) Fe and Mn concentrations, (C) P, Fe, and Mn accumulation rates.

### Diatom Reconstructions

Selected intervals from the 1990 core from site S-11 were also analyzed for fossil diatoms to reconstruct historic changes in phosphorus levels in Vadnais lake and thus provide a benchmark for goal setting on load reductions and in-lake total-P concentrations. The oldest core interval represents lake conditions just before European settlement, while three others (including the 1998 surface sample from S-11) span the period of phosphorus controls of the last two decades. Ninety-seven diatom taxa were identified in four core samples, forty of which were suitably abundant for total-P reconstruction using Ramstack's (1999) 55-Minnesota-lakes calibration model. Weighted average calibration (with and without tolerance-downweighting) was used to reconstruct historical water column total-P in the four core samples (Table 1).

Table 1. Vadnais Lake core samples and diatom-reconstructed total-P values

Sample	Core	Depth (cm)	Date (top)	Date (base)	WA recon TP $\mu\text{g L}^{-1}$	WA (tol) recon TP $\mu\text{g L}^{-1}$
1	1998	0-3	1998.8	1995.1	48.3	52.4
2	1990	0-1	1990.4	1989.4	44.2	48.6
3	1990	6-8	1984.0	1981.8	46.8	50.4
4	1990	85-90	1873	1865	38.6	31.3

These reconstruction methods indicate that the oldest sample from Vadnais Lake (ca. 1865-1873) was dominated by mesotrophic planktonic species (e.g. *Aulacoseira ambigua*) and had the lowest historical water column total-P of  $31 \mu\text{g L}^{-1}$  (Fig. 14). In contrast, the three sediment samples from the 1980s and 1990s are characterized by small *Stephanodiscus* species, clear indicators of eutrophication, and have higher reconstructed total-P values. WA reconstruction calculates values between 44 and  $48 \mu\text{g L}^{-1}$  total-P for these three recent samples, whereas tolerance downweighting shows slightly higher reconstructed values of 49 to  $52 \mu\text{g L}^{-1}$  total-P. By comparison, measured mean total-P concentrations (April-September) for these same time periods were  $60 \mu\text{g L}^{-1}$  in 1986-87,  $32 \mu\text{g L}^{-1}$  in 1987-88, and  $40 \mu\text{g L}^{-1}$  in 1996-98. Although diatom-inferred values do not track the recent (post-treatment) decline in total-P, they are generally in the right range and well within the prediction error for the model (RMSEP = 0.25 log TP).

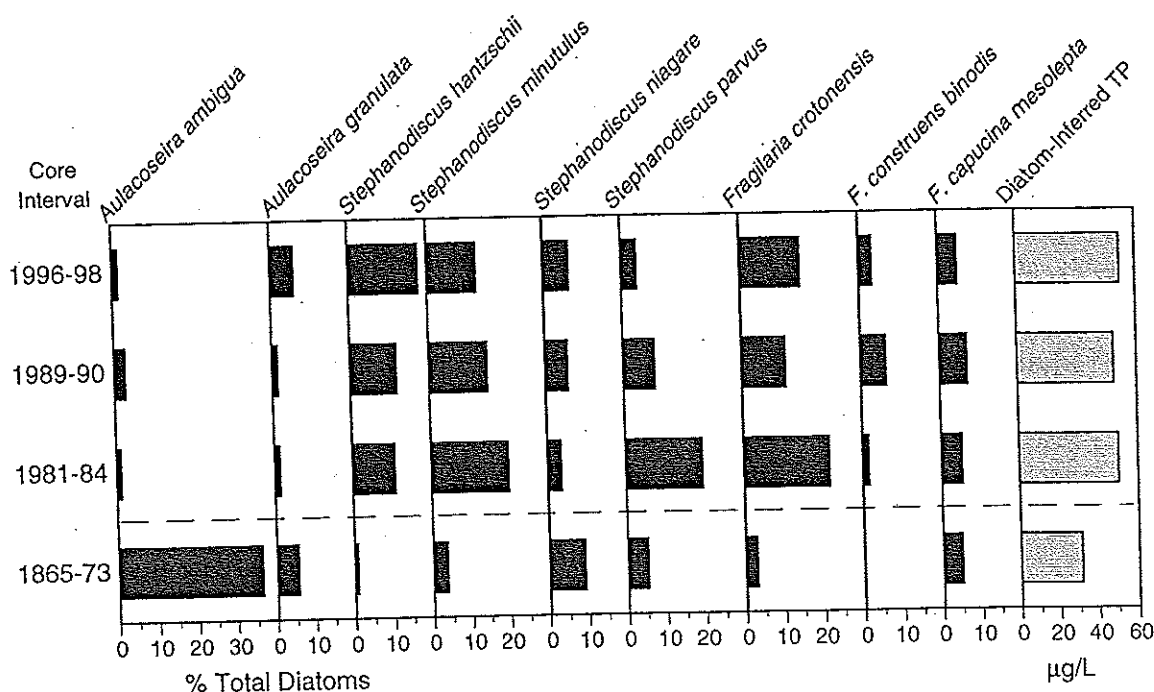


Figure 15. Vadnais Lake diatom stratigraphy. Analyst: M.B. Edlund



The diatom-inferred total-P for the mid-1800s in Vadnais Lake, though clearly lower than that for the recent decades, is at the higher end of the range of pre-settlement values reconstructed by Ramstack (1999) for 20 other metro area lakes (mean  $\pm$  s.d. =  $23 \pm 8 \mu\text{g L}^{-1}$ ). Moreover, diatom assemblages corresponding to the low total-P values of the late 1980s ( $32 \mu\text{g L}^{-1}$ ), do not look anything like those of the 1860s, suggesting as well that the diatom-inferred total-P for this period ( $31 \mu\text{g L}^{-1}$ ) is a little too high. Nonetheless, when viewed in the context of other metro-area lakes, these diatom reconstructions suggest that the management target for total-P reductions in Vadnais Lake ( $25 \mu\text{g L}^{-1}$ ) (Schuler, 1996) is very close to the pre-settlement baseline for the lake and is probably the best that might be obtained under optimal conditions.

### Littoral Sediments

Over the past decade a total of 54 metric tons of iron have been added to Lambert Creek just above its outfall to Vadnais Lake (Fig. 2). Most of this Fe is presumably transported to the lake where it sediments as a floc in the deeper, quiescent parts of the basin. However, a portion of the Fe load may also be deposited in shallow-water areas (at least temporarily until transported offshore by wave action), thereby raising Fe concentrations in littoral sediments, especially those near the mouth of Lambert Creek (Fig. 1). Concentrations of extractable Fe, as well as Mn and total-P, were measured from six sampling stations near Lambert mouth and a control region near the outfall of Vadnais Creek. Results show that Fe levels in sediments near the Lambert outfall are about ten times those from the Vadnais outfall ( $58 \pm 25 \text{ mg g}^{-1}$  vs.  $6 \pm 2 \text{ mg g}^{-1}$ ), and Mn and total-P concentrations at Lambert are 6-7 times higher (Fig. 15). However, the littoral shelf at the Lambert outfall is broader and more protected than that at Vadnais Creek, which results in a finer grain-size and higher organic content in the Lambert samples. Because amorphous iron (and associated Mn and P) is also preferentially deposited with fine-grained sediments, the higher Fe content in the Lambert outfall may represent, at least partially, differences in sediment lithology and ultimately the depositional environment of the two littoral regions. To correct for such lithological difference, Fe (Mn and P) concentrations have been normalized to organic content. These results show that Fe levels near the Lambert outfall are still about 4 times those at Vadnais Creek, while Mn and P concentrations are about 2.5 times higher.

Although these data provide fairly strong evidence that  $\text{FeCl}_3$  injections have enriched littoral sediments near the Lambert Creek outfall, it is not entirely clear whether Fe levels near Vadnais Creek provide the correct baseline for pre-injection conditions at Lambert. Although normalizing concentrations by organic content corrects for differences in depositional environment, the two streams themselves may differ in the natural (background) delivery of Fe to their respective outfalls. The Lambert flowage is substantially larger than that of Vadnais and passes through a series of wetlands, which are typically good sources for DOC as well as associated dissolved Fe (Rasmussen *et al.*, 1989). Thus littoral sediments at the Lambert outfall may receive higher background Fe loads than those in the vicinity of the Vadnais outfall. Of course, this difference would be partially offset by an expectedly higher delivery of clastic sediments and coarse detritus (with low Fe) to the Lambert littoral.

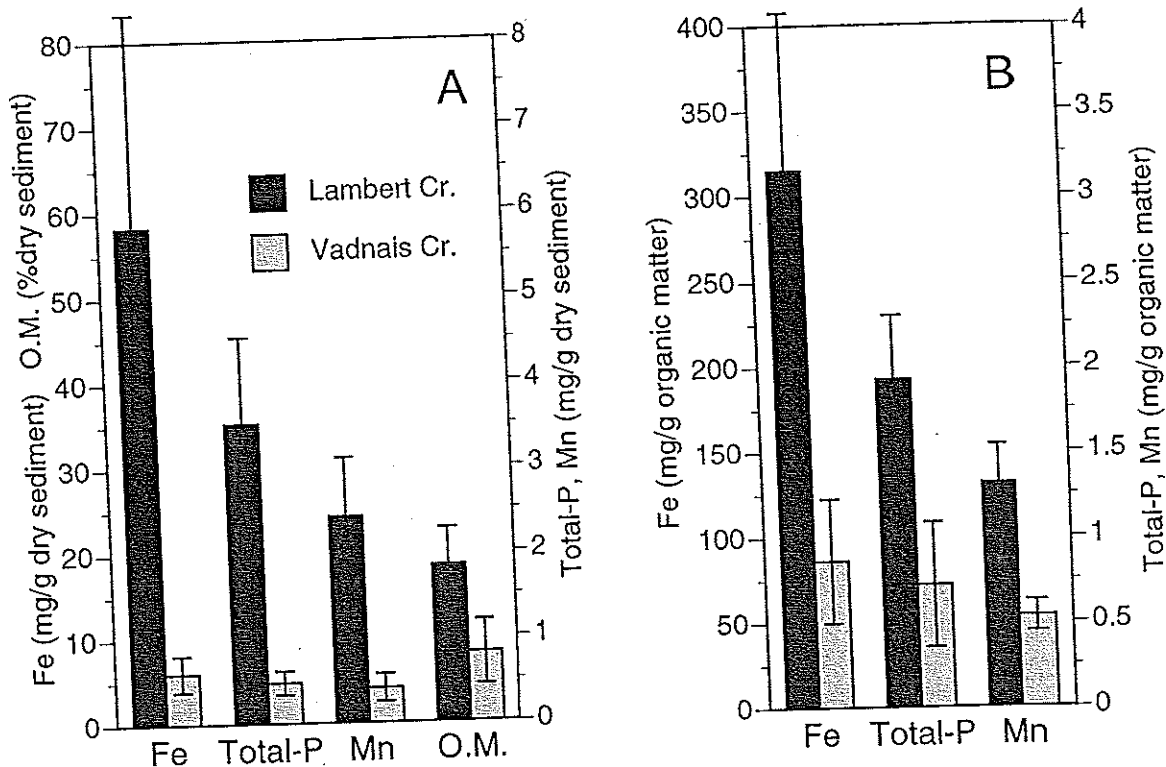


Figure 16. Chemical composition of littoral sediments from near the outfalls of Lambert and Vadnais creeks; (A) normalized to total sediment mass, (B) normalized to organic matter.

## SUMMARY AND CONCLUSIONS

- (1) Surface sediments from the deep-water regions of Vadnais Lake were sampled from a series of fixed stations on three occasions (October 1985, May 1990, and October 1988) to assess the efficacy of hypolimnetic aeration and iron injections in controlling phosphorus loading and sedimentation in the lake. Sediments were carefully sampled to a precise depth with a gravity corer, measured for total-phosphorus (and P fractions), extractable Fe and Mn, and organic content, and analyzed for  $^{210}\text{Pb}$  to estimate sediment accumulation rates. The analytical methods employed were effectively the same over the course of the study.
- (2) The lithology of Vadnais sediments is fairly uniform throughout the profundal region of the basin, being composed of an average 16% organic matter, 35% carbonate, and 49% inorganic ash. This composition changed little between sampling years, although the 1998 collections were about 2% higher in both organic matter and carbonate content. Sediment accumulation rates were also similar among sampling sites and from year to year, averaging  $1.2 \text{ kg m}^{-2} \text{ yr}^{-1}$ , although sediment fluxes at two sites nearest the hypolimnetic aerators in 1998 were about twice this rate.

- (3) Phosphorus concentrations, particularly the labile NAI-P fraction (non-apatite inorganic phosphorus) increased at almost all sites between the three sampling periods. In 1985, prior to the onset of aeration and Fe injection, total-P concentrations were uniform across the basin, averaging  $0.88 \text{ mg g}^{-1}$  dry mass. By 1990 total-P had risen to  $1.21 \text{ mg g}^{-1}$  and the NAI-P fraction had increased from 38% to 53%; this change was most apparent at sites nearest the two aerators. By 1998 total-P had increased markedly at all sites below the 12-m depth contour, rising to a lake-wide average of  $2.35 \text{ mg g}^{-1}$ , with an excess of 70% in the NAI-P fraction. These changes were accompanied by more gradual increases in extractable Fe from  $12.5 \text{ mg g}^{-1}$  in 1985 to  $16.3 \text{ mg g}^{-1}$  in 1998 and  $23 \text{ mg g}^{-1}$  in 1998.
- (4) Annual whole-basin sedimentation of total-P rose from 1.26 metric tons (t) in 1985 to 1.52 t in 1990 and 2.43 t in 1998, with virtually the entire increase represented in the NAI-P fraction. The sedimentary fluxes for 1985 and 1990 are very similar to those calculated by mass balance (the difference between measured P inflows and outflows), and the change represents a doubling of in-lake retention of external P loads (from 19% to 38%). In contrast, 1998 estimates of P sedimentation from core data were almost three times higher than those derived from mass-balance calculations. These results strongly suggest that upward diffusion of dissolved P from sediments at depth have gradually enriched surface sediments beyond that attributable to external P-loading. This diagenetic enrichment was likely enhanced by hypolimnetic aeration and iron injections, although evidence for this process from dated sediment cores is equivocal.
- (5) The increase in Fe sedimentation over the period of study is consistent with changes in external Fe inputs from iron injections, although enhanced retention from hypolimnetic aeration may also be a factor. The chemical stratigraphy of a  $^{210}\text{Pb}$ -dated, meter-long sediment core indicates that Fe concentrations in Vadnais sediments from the mid 1800s ( $36 \text{ mg g}^{-1}$ ) were considerably higher than they are today, even at the most Fe-enriched sample sites. Iron (as well as P and Mn) concentrations decrease progressively up-core, largely as a result of dilution from erosional inputs of clastic materials and increased carbonate sedimentation. Present-day Fe accumulation rates ( $24 \text{ t yr}^{-1}$ ) are about 33% greater than the mean Fe flux for the period of record ( $18 \text{ t yr}^{-1}$ ) and only 14% greater than the baseline (1860) flux of  $21 \text{ t yr}^{-1}$ . The recent increase in Fe accumulation – about  $6 \text{ t yr}^{-1}$  between 1985 and 1998 – is roughly equal to the average annual rate of Fe injections directly to Vadnais Lake.
- (6) Analysis of fossil diatoms from the dated core samples indicate that present-day phosphorus levels in Vadnais Lake are elevated well above background conditions existing in the lake prior to European settlement in the mid-1800s. Diatom-estimates of water-column total-P from recent sediments, although in the correct range, do not track measured declines in total-P over the last two decades. Pre-settlement (1860) total-P ( $31 \mu\text{g L}^{-1}$ ) reconstructed from the diatom data is at the high end of the range ( $23 \pm 8 \mu\text{g L}^{-1}$ ) for baseline total-P in 20 other metro area lakes, and may be a slight overestimate. Nonetheless, these results imply that the management target for total-P

reductions in Vadnais Lake ( $25 \mu\text{g L}^{-1}$ ) is close to the pre-settlement baseline and is probably the best that can be obtained under optimal conditions.

- (7) Littoral sediments in the region of the Lambert Creek outfall appear enriched in Fe relative to a control site near the mouth of Vadnais Creek. Collections of surface sediments from the Lambert outfall have Fe concentrations that are an order of magnitude higher than those from the Vadnais outfall as expressed on a dry-mass basis. When normalized to organic content, which reduces variability caused by differences in grain size and lithology, this difference decreases to a 4x enrichment factor. Sediments from the Lambert outfall are also higher in P and Mn than those at the Vadnais outfall, largely due to the binding of these elements to Fe. Although these results indicate that the Fe injections above the Lambert outfall (54 metric tons between 1990 and 1998) have enriched nearby littoral sediments, this area of the lake may also receive high background Fe loading from wetlands along the Lambert Creek flowage.

#### ACKNOWLEDGEMENTS

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## APPENDICES

Appendix A. Surface-sediment chemistry

Appendix B. Lead-210 surface-sediment dating and accumulation rates

Appendix C. Whole-lake chemical accumulation rates

Appendix D. Core chemical stratigraphy

Appendix E. Littoral-sediment chemistry

Appendix A. Vadnais Lake Surface-Sediment Chemistry

Sample	Total-P (mg/g)	Apatite-P (mg/g)	NAIP (mg/g)	Organic-P (mg/g)	Mn (mg/g)	Fe (mg/g)	Fe/P	Fe/Mn
<b>1998</b>								
S-1	1.102	0.159	0.445	0.498	1.64	13.25	12.03	8.07
S-2	2.390	0.139	2.059	0.191	2.94	20.07	8.40	6.83
S-3	3.321	0.118	2.482	0.721	9.35	27.96	8.42	2.99
S-4a	1.827	0.158	1.221	0.447	4.22	20.11	11.01	4.77
S-4b	2.465	0.140	1.929	0.395	6.17	24.63	9.99	3.99
S-4c	3.478	0.138	2.727	0.614	11.10	30.70	8.83	2.77
S-5	3.028	0.116	2.278	0.634	4.64	25.57	8.44	5.51
S-11	2.572	0.131	1.782	0.660	4.69	26.77	10.41	5.71
S-6	2.079	0.134	1.379	0.565	2.86	22.16	10.66	7.76
S-7a	2.576	0.175	1.899	0.502	4.52	25.24	9.80	5.59
S-7b	3.858	0.157	3.136	0.565	9.57	38.31	9.93	4.00
S-7c	3.899	0.140	3.146	0.613	10.48	36.11	9.26	3.44
S-8	2.500	0.120	1.788	0.593	4.01	25.22	10.09	6.29
S-9	1.164	0.139	0.498	0.527	1.51	16.96	14.57	11.26
S-10	1.196	0.139	0.436	0.621	1.61	13.92	11.64	8.65
Mean	2.347	0.135	1.659	0.553	4.58	23.11	10.38	6.42

<b>1990</b>								
S-1	0.810	0.195	0.297	0.317	1.96	14.39	17.78	7.35
S-2	1.130	0.132	0.514	0.484	1.36	15.06	13.32	11.07
S-3	0.987	0.127	0.455	0.406	1.96	16.55	16.76	8.46
S-4	1.558	0.124	0.965	0.469	4.99	18.66	11.98	3.74
S-5	1.017	0.128	0.426	0.463	1.42	16.49	16.21	11.60
S-11	1.720	0.134	1.102	0.484	1.92	19.26	11.20	10.03
S-6	0.990	0.132	0.401	0.457	1.79	15.93	16.10	8.91
S-7	2.630	0.123	2.071	0.436	7.98	24.70	9.39	3.10
S-8	0.771	0.139	0.227	0.405	1.40	14.15	18.34	10.08
S-9	0.888	0.140	0.316	0.432	1.25	13.43	15.12	10.73
S-10	0.857	0.170	0.270	0.417	1.23	10.51	12.26	8.55
Mean	1.214	0.140	0.640	0.434	2.48	16.28	14.41	8.51

<b>1985</b>								
S-1	0.758	0.179	0.259	0.320	1.57	8.92	11.77	5.68
S-2	0.934	0.139	0.356	0.438	1.33	13.42	14.37	10.08
S-4	0.991	0.123	0.414	0.455	1.41	14.78	14.91	10.49
S-11	0.905	0.126	0.356	0.423	1.30	13.57	14.99	10.42
S-7	0.972	0.117	0.400	0.455	1.40	14.27	14.69	10.18
S-8	0.881	0.131	0.323	0.428	1.43	13.77	15.62	9.61
S-9	0.890	0.142	0.332	0.416	1.43	12.68	14.25	8.86
S-10	0.699	0.169	0.259	0.272	1.89	8.38	11.98	4.44
Mean	0.879	0.141	0.337	0.401	1.47	12.47	14.07	8.72

Appendix B. Vadnais Lake Lead-210 Surface-Sediment Accumulation

Sample	Core Length (cm)	Age at base (years)	Cum Dry Mass (g/cm <sup>2</sup> )	210 Act. (pCi/g)	$\Delta$ 210 Act. (pCi/g)	Cum Activity (pCi/cm <sup>2</sup> )	Sed Accum (g/cm <sup>2</sup> /yr)
<b>10/14/98</b>							
S-1	3.00	3.78	0.349	6.973	0.125	2.141	0.092
S-2	3.00	3.09	0.299	9.678	0.292	2.652	0.097
S-3	3.00	2.57	0.235	10.221	0.175	2.222	0.092
S-4a	3.00	1.76	0.344	5.267	0.095	1.543	0.195
S-4b	3.00	2.84	0.331	8.206	0.245	2.450	0.116
S-4c	3.00	2.32	0.236	9.327	0.311	2.017	0.101
S-5	3.00	2.80	0.254	10.266	0.171	2.411	0.091
S-11	3.00	2.73	0.264	9.714	0.349	2.356	0.097
S-6	3.00	3.22	0.276	10.780	0.175	2.755	0.086
S-7a	3.00	1.22	0.293	4.425	0.151	1.075	0.240
S-7b	3.00	2.36	0.286	7.935	0.250	2.047	0.121
S-7c	3.00	2.51	0.269	8.847	0.262	2.172	0.107
S-8	3.00	2.77	0.261	9.956	0.179	2.390	0.094
S-9	3.00	3.03	0.309	9.234	0.279	2.600	0.102
S-10	3.00	3.78	0.340	7.140	0.228	2.141	0.090
Mean	3.00	2.72	0.290	8.531	0.219	2.198	0.115

<b>5/31/90</b>							
S-1	2.62	2.76	0.446	4.122	0.069	1.585	0.162
S-2	2.43	2.63	0.305	7.618	0.123	2.271	0.116
S-3	2.58	3.15	0.339	8.363	0.132	2.697	0.108
S-4	2.51	3.32	0.301	9.813	0.152	2.836	0.091
S-5	2.55	2.41	0.320	6.702	0.156	2.093	0.132
S-11	3.00	3.33	0.333	9.039	0.168	2.850	0.100
S-6	2.51	2.73	0.340	7.230	0.165	2.357	0.125
S-7	2.50	3.28	0.329	8.987	0.266	2.808	0.100
S-8	2.52	3.13	0.501	5.903	0.220	2.680	0.160
S-9	2.51	2.62	0.343	6.894	0.086	2.267	0.131
S-10	2.53	3.66	0.404	5.827	0.067	2.078	0.110
Mean	2.57	3.00	0.360	7.318	0.146	2.411	0.121

<b>10/16/85</b>							
S-1	3.20	3.66	0.588	4.274	0.128	2.076	0.161
S-2	2.94	3.38	0.390	7.945	0.196	2.884	0.115
S-4	2.97	3.83	0.374	9.302	0.267	3.250	0.098
S-11	2.73	3.24	0.372	7.975	0.238	2.778	0.115
S-7	3.09	3.77	0.420	8.260	0.214	3.202	0.111
S-8	3.02	3.53	0.385	8.398	0.199	3.012	0.109
S-9	3.06	3.55	0.405	8.083	0.219	3.028	0.114
S-10	3.11	4.26	0.735	4.054	0.144	2.392	0.173
Mean	3.02	3.65	0.459	7.286	0.200	2.828	0.124



Appendix C. Vadnais Lake Whole-Basin Accumulation Rates

Sample	Sed Accum kg/m <sup>2</sup> y	Total-P g/m <sup>2</sup> y	Apatite-P g/m <sup>2</sup> y	NAIP g/m <sup>2</sup> y	Organic-P g/m <sup>2</sup> y	Mn g/m <sup>2</sup> y	Fe g/m <sup>2</sup> y
<b>1998</b>							
S-1	0.92	1.02	0.15	0.41	0.46	1.52	12.23
S-2	0.97	2.31	0.13	1.99	0.19	2.84	19.42
S-3	0.92	3.04	0.11	2.27	0.66	8.56	25.60
S-4a	1.95	3.56	0.31	2.38	0.87	8.22	39.19
S-4b	1.16	2.87	0.16	2.25	0.46	7.18	28.67
S-4c	1.01	3.53	0.14	2.76	0.62	11.26	31.13
S-5	0.91	2.75	0.11	2.07	0.58	4.22	23.25
S-11	0.97	2.49	0.13	1.72	0.64	4.53	25.88
S-6	0.86	1.79	0.12	1.18	0.49	2.45	19.03
S-7a	2.40	6.19	0.42	4.56	1.21	10.86	60.65
S-7b	1.21	4.68	0.19	3.80	0.69	11.62	46.48
S-7c	1.07	4.19	0.15	3.38	0.66	11.26	38.77
S-8	0.94	2.35	0.11	1.68	0.56	3.77	23.72
S-9	1.02	1.19	0.14	0.51	0.54	1.54	17.29
S-10	0.90	1.07	0.12	0.39	0.56	1.45	12.51
Mean	1.47						

<b>1990</b>							
S-1	1.62	1.31	0.32	0.48	0.51	3.17	23.31
S-2	1.16	1.31	0.15	0.60	0.56	1.58	17.51
S-3	1.08	1.06	0.14	0.49	0.44	2.11	17.83
S-4	0.91	1.42	0.11	0.88	0.43	4.53	16.95
S-5	1.32	1.35	0.17	0.56	0.61	1.88	21.83
S-11	1.00	1.72	0.13	1.10	0.48	1.92	19.24
S-6	1.25	1.23	0.16	0.50	0.57	2.23	19.84
S-7	1.00	2.63	0.12	2.07	0.44	7.99	24.72
S-8	1.60	1.24	0.22	0.36	0.65	2.25	22.69
S-9	1.31	1.16	0.18	0.41	0.57	1.64	17.56
S-10	1.10	0.95	0.19	0.30	0.46	1.35	11.59
Mean	1.21						

<b>1985</b>							
S-1	1.61	1.22	0.29	0.42	0.51	2.53	14.33
S-2	1.15	1.08	0.16	0.41	0.51	1.54	15.49
S-4	0.98	0.97	0.12	0.40	0.44	1.38	14.44
S-11	1.15	1.04	0.14	0.41	0.48	1.49	15.55
S-7	1.11	1.08	0.13	0.45	0.51	1.56	15.89
S-8	1.09	0.96	0.14	0.35	0.47	1.56	15.01
S-9	1.14	1.01	0.16	0.38	0.47	1.63	14.43
S-10	1.73	1.21	0.29	0.45	0.47	3.26	14.47
Mean	1.24						

Appendix C. Vadnais Lake Whole-Basin Accumulation Rates

Sites	Contour	Accumulation weighted by depth contours						Fe kg/yr
		Area (m^2)	Total-P kg/yr	Apatite-P kg/yr	NAIP kg/yr	Organic-P kg/yr	Mn kg/yr	
1998								
1,9,10	3-12m	396552	433	55	173	206	594	5556
2,3,5,6,8,11	12-15m	749243	1839	88	1364	387	3294	17096
4,7	15-18m	37940	158	9	121	28	382	1549
total		1183735	2431	151	1658	622	4271	24200

<b>1990</b>								
1,2,9,10	3-12m	396552	452	91	158	203	815	6935
2,3,5,6,8,11	12-15m	749243	988	122	452	414	1495	14852
4,7	15-18m	37940	77	4	56	16	237	790
total		1183735	1517	218	665	634	2547	22577

<b>1985</b>								
1,9,10	3-12m	396552	454	98	164	193	980	5715
2,8,11	12-15m	749243	768	112	292	364	1147	11500
4,7	15-18m	37940	39	5	16	18	56	575
total		1183735	1262	215	473	574	2182	17790

Appendix D. Vadnaïs Lake Core Stratigraphy

Interval	Total-P (mg/g)	Apatite-P (mg/g)	NAIP (mg/g)	Organic-P (mg/g)	Mn (mg/g)	Fe (mg/g)	Fe/P	Fe/Mn
<b>Core-11 (90)</b>								
0-1	2.309	0.125	1.713	0.472	2.10	21.20	9.18	10.10
1-2	1.766	0.135	1.153	0.478	2.02	18.34	10.39	9.06
2-3	1.202	0.140	0.563	0.499	1.68	18.58	15.46	11.07
3-4	0.924	0.139	0.304	0.482	1.26	17.80	19.27	14.12
4-5	0.840	0.129	0.255	0.456	1.12	14.08	16.76	12.55
8-10	0.801	0.137	0.224	0.441	1.13	14.67	18.30	13.00
12-14	0.773	0.137	0.218	0.418	1.25	13.23	17.11	10.60
16-20	0.792	0.144	0.221	0.427	1.20	14.46	18.24	12.01
25-30	0.737	0.151	0.207	0.378	1.28	15.61	21.17	12.18
30-35	0.787	0.138	0.262	0.387	1.68	17.78	22.60	10.60
35-40	0.714	0.144	0.198	0.372	1.25	14.02	19.64	11.24
40-45	0.744	0.147	0.245	0.352	1.35	15.43	20.73	11.42
45-50	0.743	0.141	0.230	0.372	1.05	14.14	19.02	13.43
50-55	0.844	0.170	0.307	0.366	1.22	17.17	20.35	14.02
55-60	0.817	0.185	0.277	0.355	1.11	19.76	24.20	17.78
60-65	0.993	0.185	0.373	0.435	1.83	24.09	24.27	13.17
65-70	0.942	0.189	0.327	0.425	1.48	25.75	27.35	17.45
70-75	0.979	0.209	0.317	0.453	1.57	25.99	26.56	16.54
75-80	1.111	0.164	0.368	0.580	1.33	30.28	27.25	22.78
85-90	1.246	0.265	0.273	0.708	1.16	36.49	29.29	31.55

<b>Core-11 (98)</b>								
0-3	2.572	0.131	1.782	0.660	4.64	25.57	9.94	5.51
3-6	2.650	0.135	1.912	0.604	3.54	25.65	9.68	7.25
6-9	1.329	0.119	0.706	0.504	1.94	20.25	15.24	10.45
9-12	0.867	0.120	0.328	0.419	1.27	17.30	19.95	13.61
12-15	0.867	0.118	0.299	0.450	1.74	21.38	24.66	12.28

<b>Core-2</b>								
0-3	2.390	0.139	2.059	0.191	2.94	20.07	8.40	6.83
3-6	2.179	0.134	1.696	0.349	2.93	25.19	11.56	8.58
6-9	1.141	0.137	0.562	0.442	1.43	16.15	14.16	11.31
9-12	0.866	0.138	0.300	0.428	1.25	17.83	20.58	14.26
12-15	0.774	0.118	0.257	0.398	1.19	13.49	17.43	11.35

<b>Core-7b</b>								
0-3	3.858	1.568	3.136	0.565	9.57	38.31	9.93	4.00
3-6	4.134	1.586	3.403	0.572	9.53	36.94	8.93	3.87
6-9	4.294	1.798	3.453	0.662	12.07	43.92	10.23	3.64
9-12	4.171	1.562	3.416	0.599	9.19	38.04	9.12	4.14
12-15	4.223	1.525	3.570	0.501	11.50	40.64	9.62	3.53

Appendix E. Vadnais Lake Littoral-Sediment Chemistry

Sample	Depth (meters)	Total-P (mg/g)	Fe (mg/g)	Mn (mg/g)	%Organic	Total-P (mg/g OM)	Fe (mg/g OM)	Mn (mg/g OM)
<b>Lambert Creek</b>								
L-1	1.30	4.33	63.61	3.24	18.41	23.50	345.48	17.60
L-2	0.81	4.56	73.73	2.46	20.45	22.29	360.49	12.05
L-3	0.50	2.19	36.81	1.20	10.31	21.28	357.12	11.60
L-4	1.35	3.06	40.00	2.34	19.97	15.30	200.26	11.72
L-5	1.01	2.64	36.73	2.43	18.16	14.56	202.20	13.37
L-6	0.71	4.33	98.48	2.87	23.16	18.70	425.32	12.40
Mean		3.52	58.23	2.42	18.41	19.27	315.14	13.12
s.d.		1.01	25.07	0.69	4.36	3.73	92.55	2.28

<b>Vadnais Creek</b>								
V-1	1.85	0.57	7.89	0.48	10.67	5.36	73.99	4.52
V-2	1.45	0.62	8.41	0.52	12.30	5.04	68.37	4.27
V-3	0.90	0.53	5.99	0.48	9.47	5.61	63.28	5.10
V-4	1.68	0.46	5.00	0.51	8.37	5.52	59.68	6.05
V-5	1.48	0.45	5.99	0.35	6.32	7.07	94.78	5.53
V-6	1.17	0.23	2.42	0.10	1.55	14.52	156.15	6.63
Mean		0.48	5.95	0.41	8.11	7.19	86.04	5.35
s.d.		0.14	2.15	0.16	3.80	3.66	36.50	0.90

Samples were collected along two near-shore transects (apx. 10, 20, & 30 m from shore) at each site. Sample cores were 2 cm in length.